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OUTLINES OF METHODS OF CHEMICAL ANALYSIS

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By G. E. F. Lundell, *Chief Chemist,* and James Irvin Hoffman, *Chemist, of the National Bureau of Standards.* 250 pages. 6 by 9¼. 115 tables.

Chemical Analysis of Iron and Steel
By G. E. F. Lundell, James Irvin Hoffman, and H. A. Bright, *Chief, Section on Metal and Ore Analysis, Chemistry Division, National Bureau of Standards.* 641 pages. 6 by 9¼. 63 figures.

Applied Inorganic Analysis
By the late W. F. Hillebrand and G. E. F. Lundell. 929 pages. 6 by 9¼. 40 figures.

PUBLISHED BY
JOHN WILEY & SONS, INC.

OUTLINES OF METHODS OF CHEMICAL ANALYSIS

BY
G. E. F. LUNDELL, PH.D.
Chief Chemist, National Bureau of Standards

AND
JAMES IRVIN HOFFMAN, PH.D.
Senior Chemist, National Bureau of Standards

FIFTH PRINTING

NEW YORK
JOHN WILEY & SONS, INC.
LONDON: CHAPMAN & HALL, LIMITED

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Fifth Printing, March, 1948

Printed in U. S. A.

PREFACE

In researches on chemical analysis during the past fifty years there has been an ever-increasing tendency to put the cart before the horse, to concentrate on the final act of an analysis, the *determination*, at the expense of *chemical analysis* itself. As a result, there is no lack of excellent methods for the determination of the elements *when they occur alone.* On the other hand, there has been no corresponding advance in methods of chemical separations or in methods of determination that can be applied to mixtures of the elements.

This one-sided development of chemical analysis is perfectly natural. In the field of pure chemical analysis, problems are so enormously simplified by confining studies to single elements or to simple systems that it is natural to follow the line of least resistance. In the field of applied analysis, there is such pressure for speed and economy that the chief concern lies in the development of methods that are satisfactory for the material in hand. Such methods must necessarily be more versatile than those usually studied in pure analysis, but are developed to meet a special rather than the general case.

As more and more elements come into general use, and materials to be analyzed grow more and more complex, the narrow viewpoint of a chemical determination becomes more and more precarious and leads to ever-growing difficulties. In this book, therefore, an attempt has been made to feature *chemical analyses* rather than *chemical determinations.*

The chief aims might be briefly summarized as (1) to furnish analysts with information concerning the behavior of all the elements in the more important reactions that are used in analytical chemistry; (2) to stimulate searches for more selective reagents; (3) to enlighten chemists who hold chemical analysis in too light regard; and (4) to inform non-chemists concerning the complexities and difficulties that beset the analyst.

As the title indicates, detailed descriptions of procedures and extensive references to the literature have been omitted. This has been done in order to keep the treatment as simple and concise as possible, and to avoid duplication of matter already contained in "Applied Inorganic Analysis" by Hillebrand and Lundell. Each text supplements the other, and in future revisions it is planned to make the bond still closer.

The authors are painfully aware that the task is stupendous, and that they are exhibiting considerable temerity in attempting to perform it. Any treatment must necessarily be far from complete at the start, and so they will be most grateful for advice concerning errors of commission or omission.

Grateful acknowledgment is made to our associates at the National Bureau of Standards, particularly Mr. J. A. Scherrer, Mr. H. B. Knowles, Mr. H. A. Bright, Dr. E. Wichers, Dr. R. Gilchrist, and Mr. B. F. Scribner.

G. E. F. LUNDELL
JAMES I. HOFFMAN

WASHINGTON, D. C.
April, 1937

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OUTLINES OF
METHODS OF CHEMICAL ANALYSIS

PART I. GENERAL CONSIDERATIONS

CHAPTER I

INTRODUCTION

A. Introduction

Chemical analysis does not differ from other fields of endeavor in which one works with hand as well as brain. In other words, the chief requisites for success are knowledge coupled with a keen sense of observation, tools, and skill.

Skill deals with the mechanical operations of chemical analysis, and must be built on natural aptitude plus training. Skill becomes increasingly important as the need for precision rises, and is therefore the most important consideration in routine determinations that are made by a prescribed method.[1] In applied chemical analysis, skill does not lose its importance, but here it is distinctly secondary to knowledge.

The analyst has little cause for complaint concerning the physical tools that are at his command. In general, it can be said that these are more than satisfactory for his present needs. With but few restrictions the same can be said of minor chemical tools such as reagents. It is the chief chemical tools, the chemical reactions upon which chemical determinations are based, that cause the analyst the greatest concern. These have not kept pace with the development of the other tools, for discoveries of new and useful reactions have been few and far between. This is a most serious obstacle to accurate chemical analyses of everyday materials, for determinations must still be made by reactions that are shared or affected by substances other than the one under consideration. A method for the determination of molybdenum that will yield results that are accurate to one part in five thousand in tests of pure ammonium molybdate may not give an accuracy of one part in ten when applied to a molybdenum ore such as wulfenite.

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[1] Strictly speaking, " determination " refers specifically to the method whereby the amount of the element or constituent in question is actually found, while " analysis " refers to all the operations that may be required to permit the use of the method of determination. The number and the complexity of the operations depend on the selectivity of the method of determination, and on the composition of the material under test. Thus, the method in which alumina is determined by precipitating with ammonium hydroxide, filtering, igniting, and weighing as Al_2O_3 can be applied directly in tests of pure ammonium alum, while with bauxite so many operations are required that the precipitation by ammonium hydroxide is but little more than an incident (see page 186). The same operations serve in the determination of a given constituent in materials of similar composition, and when once developed form the basis of so-called " routine " determinations.

Any determination in applied chemical analysis is dependent on a knowledge of the behavior of the elements in the reaction upon which the determination is based. This in turn demands knowledge of the composition of the material under test. One does not need to know *all* of the constituents, but one must have knowledge of those that would interfere if present. Until truly selective reactions have been developed, this knowledge must be brought into play with each new type of material that is encountered. Its comprehensiveness, more than any other factor, spells success or failure in the determination.

Finally, a keen sense of observation must be coupled with knowledge, for this is not only necessary to warn of danger on the chosen path, but also to discover other paths that may be followed with profit.

B. Chemical Analysis

Methods of chemical analysis serve the very interesting and useful purpose of enabling the analyst to find out what chemical elements or compounds are present in a given material, and how much of each constituent is present. Methods for determining the composition of materials are classified as qualitative methods of analysis. Methods for determining the percentage composition of materials are classified as quantitative methods. Both are based on differences in the behavior of elements or their compounds.

In qualitative analysis the underlying aims are to separate the constituent that is sought from anything that would interfere with its detection, and to avoid such losses of the constituent as would endanger the test. In quantitative analysis all the constituent must be separated from everything that would interfere with its determination. Both branches of analysis present extremes of complexity, ranging from simple direct tests such as the dimethylglyoxime reaction for the detection or determination of nickel to the laborious separations that are necessary with tantalum or the rare earths.

In the early days of chemistry, the compositions of substances were unknown. Common salt was used for centuries before it was demonstrated that it is composed of the two elements sodium and chlorine. As fast as a new element was isolated and identified, it was natural that a search should be made for it in the compounds that occur in nature or had been made by man. Whenever it was found, the next step was always to find out how much of it was present.

There is no such widespread need of qualitative testing today, for we know what to expect in the usual case. An igneous rock will surely contain silicon, aluminum, iron, calcium, magnesium, sodium, and potassium, and the analyst knows that he can probably find small amounts of elements such as manganese, titanium, zirconium, and vanadium if he takes large enough samples. A qualitative search for *all* the elements that are present is therefore rarely, if ever, made as a preliminary step in quantitative analysis. Tests are occasionally performed before a determination is attempted in order to make sure of the absence of substances that would interfere in the method that is to be employed. In this case a simple direct test is chosen if possible, as for example the purplish-colored permanganic acid which manganese gives when a nitric acid solution of its nitrate is treated with sodium bismuthate. If the analyst has no idea as to the composition of the material under test, he must apply such qualitative tests as will give him the information that he needs. Here, much time is often saved by first testing for groups of elements, for, if a negative test for the group is obtained, there is obviously no need to test for each of the numerous members of the group. Of the greatest aid in qualitative testing are chemical microscopy and spectrochemical and X-ray methods.

As a matter of fact, qualitative tests are made more often at the end than at the start of an analysis. These are made if there is reason to question the purity or identity of the final product. If tungsten has been determined by weighing it as the oxide, WO_3, the analyst usually examines the oxide to make sure that possible contaminating elements such as iron, molybdenum, tin, columbium, or tantalum are absent.

It has frequently been said that the best qualitative test is a quantitative test. Very often it takes little more time, and results are more certain if a proper quantitative method is used in the search.

Quantitative analyses can be made by a variety of methods. Chief among these are the gravimetric and volumetric procedures. In the former, the constituent is weighed after it has been separated so far as practicable from its fellows. In volumetric procedures, the constituent is obtained in solution, and then made to undergo a definite change by the measured addition of a solution of known reacting power. Gravimetric methods have the advantage of enabling the analyst to see the constituent, and the disadvantage of being more or less time-consuming. Volumetric methods, which are usually at least as accurate as gravimetric methods, have the advantage of being rapid, and the disadvantage of often giving no indication of the presence of the constituent other than the consumption of the reacting solution. This is of especial significance because probably no method of chemical determination, whether it be gravimetric or volumetric, is based on a reaction that is peculiar to a single compound.

In the early days, methods of chemical analysis were exclusively gravimetric. Today a large percentage of analyses are made by volumetric methods. The development of electrometric methods of determining end points has particularly increased the use of volumetric methods. Both gravimetric and volumetric methods are continually changing as improvements or more selective reagents are discovered. In the great field of applied inorganic analysis, where economy of time and effort is of prime importance, the constant aim is to develop selective methods that are not affected by constituents other than the one in question, and hence require a minimum number of operations. Coupled with this, of course, is the use of a separate sample for each constituent that is to be determined.

Finally, it should be noted that more and more use is being made of supplementary methods such as those of microanalysis and chemical microscopy, and of physical methods such as those based on X-ray phenomena or emission or absorption spectra.

C. Periodic Arrangement of the Elements

Excluding possible degradation stages of the radioactive elements, the maximum number of elements that the analyst can encounter is 92. Some of these he will probably never encounter unless he is engaged in special work. The distribution of the elements in ordinary materials is outlined in Chapter II.

Discussions of the occurrences, properties, and reactions of the elements are so enormously simplified by referring to a table in which they have been arranged according to their properties that this treatment has been adopted throughout the book. In the tables most commonly used an attempt is made to group the elements according to *valence.* This leads to strange bedfellows, and introduces the need of conventions, such as subgroup I and subgroup II within a group. From the chemist's, particularly the analyst's, viewpoint it is much more rational and satisfactory to group the elements in accordance with the *structure* of their atoms. This leads to a simpler grouping as well as to less congestion.

The authors have therefore chosen the periodic arrangement of the elements shown in Table 1. In this table the elements are arranged horizontally in seven periods which are in accordance with the *number* of their electrons (atomic number), and of the *shells* in which the electrons are located. The vertical (group) arrangement is in accordance with the type of electrons and their *distribution* in the incompleted shells.

TABLE 1

Periodic Chart of the Elements

Elements grouped according to the number, type, and distribution of the electrons in their atoms
(Atomic number of each element is shown in upper right-hand corner.)

SHELLS		DISTRIBUTION OF VALENCE ELECTRONS IN SHELLS																	NO VALENCE ELECTRONS	NUMBER OF ELECTRONS IN COMPLETED SHELLS						
TOTAL NUMBER	DESIGNATION OF OUTER SHELL	ALL VALENCE ELECTRONS LOCATED IN OUTER SHELL		VALENCE ELECTRONS DISTRIBUTED IN OUTER AND NEXT INNER SHELLS								ALL VALENCE ELECTRONS LOCATED IN OUTER SHELL								K	L	M	N	O	P	Q
1	K	H^{1}																	He^{2}	2						
2	L	Li^{3}	Be^{4}											B^{5}	C^{6}	N^{7}	O^{8}	F^{9}	Ne^{10}	2	8					
3	M	Na^{11}	Mg^{12}											Al^{13}	Si^{14}	P^{15}	S^{16}	Cl^{17}	A^{18}	2	8	8				
4	N	K^{19}	Ca^{20}	Sc^{21}	Ti^{22}	V^{23}	Cr^{24}	Mn^{25}	Fe^{26}	Co^{27}	Ni^{28}	Cu^{29}	Zn^{30}	Ga^{31}	Ge^{32}	As^{33}	Se^{34}	Br^{35}	Kr^{36}	2	8	18	8			
5	O	Rb^{37}	Sr^{38}	Y^{39}	Zr^{40}	Cb^{41}	Mo^{42}	—^{43}	Ru^{44}	Rh^{45}	Pd^{46}	Ag^{47}	Cd^{48}	In^{49}	Sn^{50}	Sb^{51}	Te^{52}	I^{53}	Xe^{54}	2	8	18	18	8		
6	P	Cs^{55}	Ba^{56}	*La^{57}	Hf^{72}	Ta^{73}	W^{74}	Re^{75}	Os^{76}	Ir^{77}	Pt^{78}	Au^{79}	Hg^{80}	Tl^{81}	Pb^{82}	Bi^{83}	Po^{84}	—^{85}	Rn^{86}	2	8	18	32	18	8	
7	Q	—^{87}	Ra^{88}	Ac^{89}	Th^{90}	Pa^{91}	U^{92}													2	8	18	32	18	†12	†2

† SHELLS INCOMPLETED

* ELEMENTS 58-71	Ce^{58}	Pr^{59}	Nd^{60}	—^{61}	Sm^{62}	Eu^{63}	Gd^{64}	Tb^{65}	Dy^{66}	Ho^{67}	Er^{68}	Tm^{69}	Yb^{70}	Lu^{71}	VALENCE ELECTRONS DISTRIBUTED IN OUTER AND NEXT TWO INNER SHELLS

Heavy solid blocks inclose elements whose valence electrons are of the *s* type.

Heavy broken blocks inclose elements whose valence electrons are entirely of the *s d* type.

* Elements of atomic numbers 58 to 71 are placed in this group because they show remarkable similarities to scandium, yttrium, and lanthanum in both physical and chemical properties. Thus, all have the same electron structure in the outer and next inner shells, all are trivalent in their principal valences, all form basic oxides, and all yield oxalates and fluorides that are difficultly soluble in diluted acids. They are sometimes called the " rare earth elements." This term is unsatisfactory, for some of the elements are no longer rare, and there is by no means universal agreement as to whether it refers to elements 58–71, or to all the elements which form fluorides and oxalates that are insoluble in dilute mineral acids.

Light solid blocks inclose elements whose valence electrons are entirely of the *s p* type.

Light broken blocks inclose elements whose valence electrons are of the *s d f* type.

Elements not inclosed in blocks are those which have no valence electrons.

Elements of atomic numbers 43, 61, 85, and 87 have not yet been isolated, although indications of their existence have been claimed.

Atomic number is the most fundamental fact concerning an atom. It denotes numerically the net positive charge (protons) in the atomic nucleus, and is therefore equal to the number of negative charges (electrons) surrounding the nucleus of a neutral atom.[2] If the elements are arranged in order of increasing atomic number, they form an integer series from H = 1 to U = 92. However, certain chemical (e.g., valence), physical (e.g., atomic volumes), and optical (e.g., spectral structures) properties have long been known to show periodicities in the sequence of chemical elements, so that the entire series is divided into 7 periods, with 2 elements in the first, 8 in the second, 8 in the third, 18 in the fourth, 18 in the fifth, 32 in the sixth, and the remainder in the seventh. Each period begins with a univalent element, and, in general, the maximum valence of the elements in the period increases to a certain limiting value, and then repeats itself.

Studies in Röntgen and optical spectra have given physical significance to the periodic recurrence of properties of the elements and show (1) that the periods correspond to the number of shells (referring to the Bohr atom) in which the electrons are located, (2) that the electrons differ in type, and (3) that elements having similar properties have, in general, the same number and type of electrons in their incompleted shells. The shells are seven in number and are often referred to as the *K*, *L*, *M*, *N*, *O*, *P*, and *Q* shells. The electrons exhibit four types of orbital momentum. These types have been characterized as sharp, principal, diffuse, and fundamental, and are now symbolized by the initials *s*, *p*, *d*, and *f*.

Elements occurring in the same period all have the same number and kind of shells, those of the first period having only the *K* shell, the second an inner *K* shell and an outer *L* shell, and so on. As the electrons enter an incompleted shell, the first two are always of the *s* type, the next six of the *p*, the next ten of the *d*, and the next 14 of the *f* type. The smallest number of electrons in a single shell is one (that of the *K* shell of hydrogen), and the largest number of electrons (that of the *N* shell of elements 71–92) is 32. The completion of the outer structure is in each period characterized by the formation of a noble gas of chemical inertness and high stability.

The valence of an element is governed by the electrons in its incompleted shells. The *s* and *p* type of valence electrons are always located in the outer incompleted shell. Valence electrons of the *d* type are always

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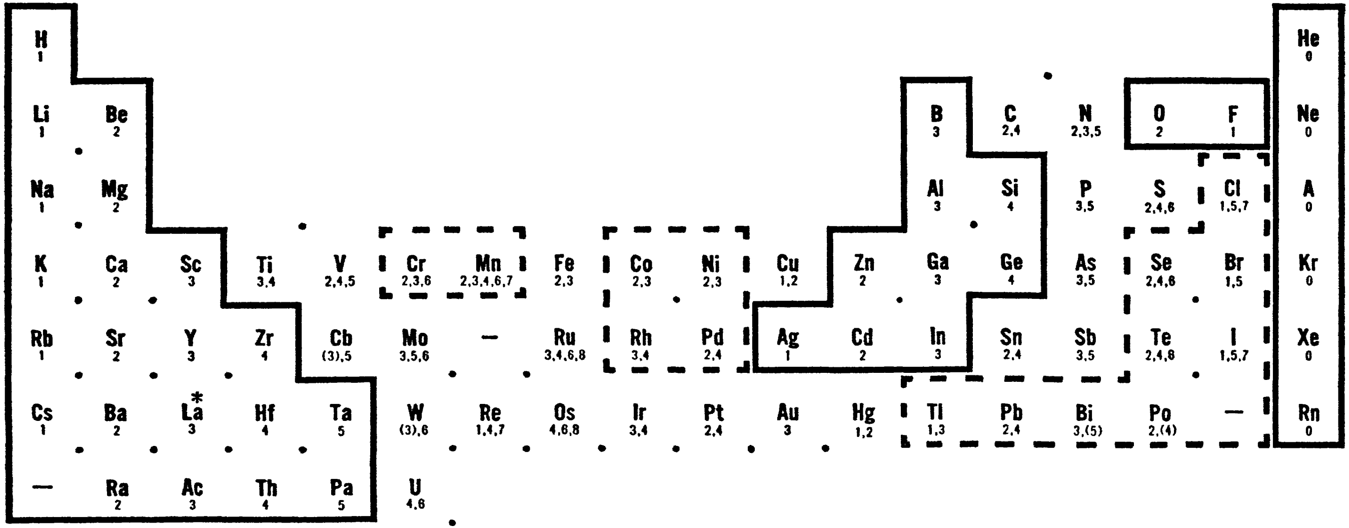
[2] The nucleus may contain one or more neutrons in addition to protons. These increase the mass of the atom, but do not in any known way affect the chemical reactions of the element. Such atoms constitute isotopic forms of the element. The accepted atomic weight of an isotopic element represents the average of the atomic weights of a mixture of its isotopes. This will represent the "atomic weight" of the naturally occurring element if the proportions of the isotopes are not disturbed in preparing the sample on which the determination of the atomic weight was made. If the proportions are disturbed, as by fractional distillation, the "atomic weight" is that of an unknown mixture of isotopes.

TABLE 2

Valences of the Elements in Analytical Procedures



H 1																	He 0
Li 1	Be 2											B 3	C 2,4	N 2,3,5	O 2	F 1	Ne 0
Na 1	Mg 2											Al 3	Si 4	P 3,5	S 2,4,6	Cl 1,5,7	A 0
K 1	Ca 2	Sc 3	Ti 3,4	V 2,4,5	Cr 2,3,6	Mn 2,3,4,6,7	Fe 2,3	Co 2,3	Ni 2,3	Cu 1,2	Zn 2	Ga 3	Ge 4	As 3,5	Se 2,4,6	Br 1,5	Kr 0
Rb 1	Sr 2	Y 3	Zr 4	Cb (3),5	Mo 3,5,6	—	Ru 3,4,6,8	Rh 3,4	Pd 2,4	Ag 1	Cd 2	In 3	Sn 2,4	Sb 3,5	Te 2,4,6	I 1,5,7	Xe 0
Cs 1	Ba 2	La* 3	Hf 4	Ta 5	W (3),6	Re 1,4,7	Os 4,6,8	Ir 3,4	Pt 2,4	Au 3	Hg 1,2	Tl 1,3	Pb 2,4	Bi 3,(5)	Po 2,(4)	—	Rn 0
—	Ra 2	Ac 3	Th 4	Pa 5	U 4,6												

* Also elements 58–71. All these are normally trivalent, although some may occur in other valences that are useful in analysis, as for example cerium (quadrivalent), and europium and ytterbium (divalent).

The noble gases are given zero valence because they do not form compounds. The valences of the other elements are those encountered in their *compounds*, and do not include the zero valence of such elements as may be obtained or used in the elemental state. For negative valences consult Table 5.

Elements inclosed in *heavy* solid blocks show only the indicated valence in reactions that are used by the analyst. All the other elements are encountered in two or more valences as indicated.

Elements that are not inclosed in blocks can be converted to their highest indicated valence by oxidizing with nitric acid alone, but complete oxidation of ruthenium is difficult.

Of the elements in the *broken blocks*, only thallium and palladium (mixture of Pd^{II} and Pd^{IV}) can be oxidized to their highest indicated valences by treatment with aqua regia. The others require special treatments.

located in the next inner incompleted shell, while those of the *f* type are found only in the atoms of elements of atomic numbers 58–71, and in these they are located in the second inner shell.

With but few exceptions (Cr, Cb, Mo, Ru, Rh, Pd, Pt, and elements 58–71) the incompleted shells of *normal* atoms of elements in the same group exhibit the same structure as to type, number of each type, and total number of electrons. Elements 58–71 resemble scandium, yttrium, and lanthanum in the structure of their incompleted outer (*P*) and next inner (*O*) shells, and differ only in the introduction of the 4 *f*-type electrons in their second inner (*N*) incompleted shell. It is quite possible that in their chemical combinations with other elements the normal atoms of the other exceptional elements enter into metastable states having structures that conform with the other elements of their groups.

D. Valences of the Elements

In Table 2 are shown the valences that are exhibited by the elements in the procedures which the analyst commonly uses for their determination. It will be noted that more than one-half of the elements will be encountered in only one valence. Of those that may be encountered in more than one valence, one element (manganese) may be encountered in five, one (ruthenium) in four, a few in three, and the remaining elements in two valences. The indicated valences are those which are of interest to the analyst, and do not necessarily include all the valences that the elements may exhibit in general reactions.

E. Colors of the Compounds of the Elements

The elements that form colored compounds, and the types of compounds that are apt to be colored, are shown in Table 3. The colored compounds are of the greatest help to the analyst, and serve in quantitative as well as qualitative methods.

F. Alphabetical Arrangement of the Elements

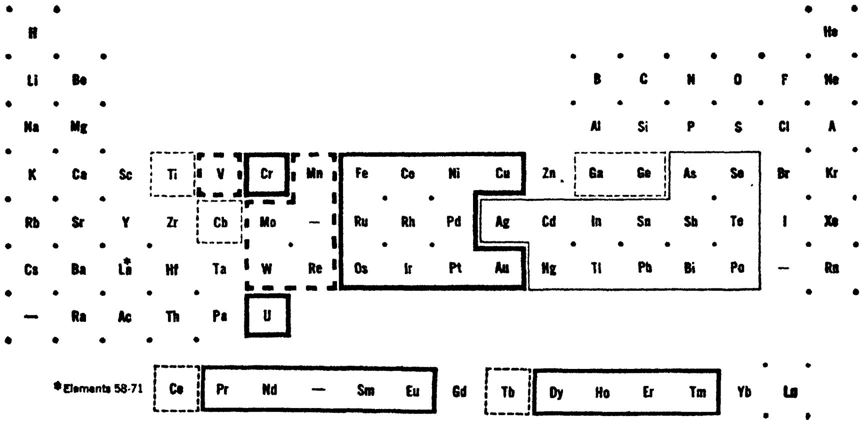
Elements to which atomic weights have been assigned are listed alphabetically in Table 4, together with their symbols and atomic weights. Eighty-six of the elements are included, the missing ones being actinium, polonium, and the four elements (43, 61, 85, and 87) which have not been isolated as yet.

G. Arrangement of the Elements in the Order of Their Atomic Numbers

In Table 5, the elements are listed in the order of their atomic numbers, together with the isotopes that have been recognized. Data already given in Tables 2 and 4 are repeated for the sake of convenience and of intercomparison.

TABLE 3

Colors of Chemical Compounds


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U
*Elements 58-71 Ce Pr Nd — Sm Eu Gd Tb Dy Ho Er Tm Yb Lu

Heavy solid blocks inclose elements whose compounds are almost always colored.

Heavy broken blocks inclose elements whose compounds are often colored.

Light solid blocks inclose elements whose colored compounds are confined chiefly to those in the solid state.

Light broken blocks inclose elements whose colored compounds are chiefly those of abnormal valence.

Elements not in blocks are those whose compounds are nearly always colorless.

Elements in the first class (compounds almost always colored) yield colored oxides and sulphides, colored salts with " colorless " acids such as hydrochloric acid, and colored solutions of these salts.

Elements in the second class (compounds often colored) yield colored sulphides and oxides (except MoO_3). In their salts and solutions of their salts they show no regular behavior. Thus, tungstic oxide is yellow, and sodium tungstate is colorless in either solid or dissolved state, ammonium metavanadate is colorless, and a solution of it in hydrochloric acid is yellow, while manganese sulphate is pink in the solid and colorless (in moderate concentration) in the dissolved state.

Elements in the third class (colored compounds confined chiefly to those in the solid state) all yield colored sulphides, some yield colored oxides, and some yield colored iodides. Their dissolved compounds, as for example chlorides, sulphates, and nitrates, are usually colorless.

Elements in the fourth class (colored compounds chiefly those of abnormal valence) yield colorless compounds when present in their normal valence. If the valence is changed, colored compounds may ensue, as the change from colorless to yellow with cerous to ceric sulphate, and colorless to violet with titanic to titanous sulphate.

Elements in the fifth class (compounds nearly always colorless) are (1) the elements which are basic and yield colorless oxides and colorless salts with "colorless" acids, and (2) the elements which are acidic and yield colorless salts with the "colorless bases."

TABLE 4
International Atomic Weights*
1937

	Symbol	Atomic Number	Atomic Weight		Symbol	Atomic Number	Atomic Weight
Aluminum	Al	13	26.97	Molybdenum	Mo	42	96.0
Antimony	Sb	51	121.76	Neodymium	Nd	60	144.27
Argon	A	18	39.944	Neon	Ne	10	20.183
Arsenic	As	33	74.91	Nickel	Ni	28	58.69
Barium	Ba	56	137.36	Nitrogen	N	7	14.008
Beryllium	Be	4	9.02	Osmium	Os	76	191.5
Bismuth	Bi	83	209.00	Oxygen	O	8	16.0000
Boron	B	5	10.82	Palladium	Pd	46	106.7
Bromine	Br	35	79.916	Phosphorus	P	15	31.02
Cadmium	Cd	48	112.41	Platinum	Pt	78	195.23
Calcium	Ca	20	40.08	Potassium	K	19	39.096
Carbon	C	6	12.01	Praseodymium	Pr	59	140.92
Cerium	Ce	58	140.13	Protoactinium	Pa	91	231
Cesium	Cs	55	132.91	Radium	Ra	88	226.05
Chlorine	Cl	17	35.457	Radon	Rn	86	222
Chromium	Cr	24	52.01	Rhenium	Re	75	186.31
Cobalt	Co	27	58.94	Rhodium	Rh	45	102.91
Columbium	Cb	41	92.91	Rubidium	Rb	37	85.48
Copper	Cu	29	63.57	Ruthenium	Ru	44	101.7
Dysprosium	Dy	66	162.46	Samarium	Sm	62	150.43
Erbium	Er	68	167.64	Scandium	Sc	21	45.10
Europium	Eu	63	152.0	Selenium	Se	34	78.96
Fluorine	F	9	19.00	Silicon	Si	14	28.06
Gadolinium	Gd	64	156.9	Silver	Ag	47	107.880
Gallium	Ga	31	69.72	Sodium	Na	11	22.997
Germanium	Ge	32	72.60	Strontium	Sr	38	87.63
Gold	Au	79	197.2	Sulphur	S	16	32.06
Hafnium	Hf	72	178.6	Tantalum	Ta	73	180.88
Helium	He	2	4.002	Tellurium	Te	52	127.61
Holmium	Ho	67	163.5	Terbium	Tb	65	159.2
Hydrogen	H	1	1.0078	Thallium	Tl	81	204.39
Indium	In	49	114.76	Thorium	Th	90	232.12
Iodine	I	53	126.92	Thulium	Tm	69	169.4
Iridium	Ir	77	193.1	Tin	Sn	50	118.70
Iron	Fe	26	55.84	Titanium	Ti	22	47.90
Krypton	Kr	36	83.7	Tungsten	W	74	184.0
Lanthanum	La	57	138.92	Uranium	U	92	238.07
Lead	Pb	82	207.21	Vanadium	V	23	50.95
Lithium	Li	3	6.940	Xenon	Xe	54	131.3
Lutecium	Lu	71	175.0	Ytterbium	Yb	70	173.04
Magnesium	Mg	12	24.32	Yttrium	Y	39	88.92
Manganese	Mn	25	54.93	Zinc	Zn	30	65.38
Mercury	Hg	80	200.61	Zirconium	Zr	40	91.22

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* J. Am. Chem. Soc. **59**, 225 (1937).

TABLE 5

The Elements and Their Atomic Numbers, Symbols, Atomic Weights, Isotopes, and Valences of Interest to the Analyst

Atomic Number	Element	Symbol	Atomic Weight*	Isotopes†	Most Stable Valence	Valences Useful in Chemical Analysis
1	Hydrogen	H	1.0078	1, 2, 3	1	1
2	Helium	He	4.002	4	0	0
3	Lithium	Li	6.940	7, 6	1	1
4	Beryllium	Be	9.02	9, (8)	2	2
5	Boron	B	10.82	11, 10	3	3
6	Carbon	C	12.01	12, 13	4	±4, 2
7	Nitrogen	N	14.008	14, 15	−3	−3, 5, 2
8	Oxygen	O	16.0000	16, 18, 17	2	2
9	Fluorine	F	19.00	19	−1	−1
10	Neon	Ne	20.183	20, 22, 21	0	0
11	Sodium	Na	22.997	23	1	1
12	Magnesium	Mg	24.32	24, 25, 26	2	2
13	Aluminum	Al	26.97	27	3	3
14	Silicon	Si	28.06	28, 29, 30	4	4
15	Phosphorus	P	31.02	31	5	5, ±3
16	Sulphur	S	32.06	32, 34, 33	6	6, 4, −2
17	Chlorine	Cl	35.457	35, 37	−1	±1, 7, 5
18	Argon	A	39.944	40, 36, 38	0	0
19	Potassium	K	39.096	39, 41, 40	1	1
20	Calcium	Ca	40.08	40, 44, 42, 43	2	2
21	Scandium	Sc	45.10	45	3	3
22	Titanium	Ti	47.90	48, 46, 47, 50, 49	4	4, 3
23	Vanadium	V	50.95	51	5	5, 4, 2
24	Chromium	Cr	52.01	52, 53, 50, 54	3	6, 3, 2
25	Manganese	Mn	54.93	55	2	7, 4, 2, 6, 3
26	Iron	Fe	55.84	56, 54, 57, 58	3	3, 2
27	Cobalt	Co	58.94	59	2	3, 2
28	Nickel	Ni	58.69	58, 60, 62, (61), 64	2	2, 3
29	Copper	Cu	63.57	63, 65	2	2, 1
30	Zinc	Zn	65.38	64, 66, 68, 67, 70	2	2
31	Gallium	Ga	69.72	69, 71	3	3
32	Germanium	Ge	72.60	74, 72, 70, 73, 76	4	4
33	Arsenic	As	74.91	75	3	5, ±3
34	Selenium	Se	78.96	80, 78, 76, 82, 77, 74	4	6, 4, −2
35	Bromine	Br	79.916	79, 81	−1	±1, 5
36	Krypton	Kr	83.7	84, 86, 82, 83, 80, 78	0	0
37	Rubidium	Rb	85.48	85, 87	1	1
38	Strontium	Sr	87.63	88, 86, 87	2	2
39	Yttrium	Y	88.92	89	3	3
40	Zirconium	Zr	91.22	90, 92, 94, 91, 96	4	4
41	Columbium	Cb	92.91	93	5	5, (3)
42	Molybdenum	Mo	96.0	98, 96, 95, 92, 94, 100, 97	6	6, 3, 5
43						
44	Ruthenium	Ru	101.7	102, 101, 104, 100, 99, 96, (98)	$3 \rightleftarrows 4$	8, 3, 4, 6
45	Rhodium	Rh	102.91	103	3	3, 4
46	Palladium	Pd	106.7	104, 105, 106, 108, 110, 102	2	2, 4
47	Silver	Ag	107.880	107, 109	1	1
48	Cadmium	Cd	112.41	114, 112, 110, 111, 113, 116, 106, 108	2	2
49	Indium	In	114.76	115, 113	3	3
50	Tin	Sn	118.70	120, 118, 116, 119, 117, 124, 122, 112, 114, 115	4	4, 2
51	Antimony	Sb	121.76	121, 123	3	5, ±3

TABLE 5 — *Continued*

Atomic Number	Element	Symbol	Atomic Weight*	Isotopes†	Most Stable Valence	Valences Useful in Chemical Analysis
52	Tellurium	Te	127.61	130, 128, 126, 125, 124, 122, 123	4	6, 4, −2
53	Iodine	I	126.92	127	−1	5, 7, −1
54	Xenon	Xe	131.3	129, 132, 131, 134, 136, 130, 128, 126, 124	0	0
55	Cesium	Cs	132.91	133	1	1
56	Barium	Ba	137.36	138, 137, 136, 135	2	2
57	Lanthanum	La	138.92	139	3	3
58	Cerium	Ce	140.13	140, 142	3	4, 3
59	Praseodymium	Pr	140.92	141	3	3
60	Neodymium	Nd	144.27	142, 144, 146, 143, 145	3	3
61						
62	Samarium	Sm	150.43	152, 154, 147, 149, 148, 150, 144	3	3
63	Europium	Eu	152.0	151, 153	3	3, 2
64	Gadolinium	Gd	156.9	158, 156, 155, 157, 160	3	3
65	Terbium	Tb	159.2	159	3	3
66	Dysprosium	Dy	162.46	164, 163, 162, 161	3	3
67	Holmium	Ho	163.5	165	3	3
68	Erbium	Er	167.64	166, 168, 167, 170	3	3
69	Thulium	Tm	169.4	169	3	3
70	Ytterbium	Yb	173.04	174, 172, 173, 176, 171	3	3, 2
71	Lutecium	Lu	175.0	175	3	3
72	Hafnium	Hf	178.6	180, 178, 177, 179, 176	4	4
73	Tantalum	Ta	180.88	181	5	5
74	Tungsten	W	184.0	184, 186, 182, 183	6	6, (3)
75	Rhenium	Re	186.31	187, 185	7	7, 4, −1
76	Osmium	Os	191.5	192, 190, 189, 188, 186, 187	4	8, 4, 6
77	Iridium	Ir	193.1	193, 191	$3 \rightleftarrows 4$	3, 4, 6
78	Platinum	Pt	195.23	196, 195, 194, 198, 192	4	4, 2
79	Gold	Au	197.2	197	3	3
80	Mercury	Hg	200.61	202, 200, 199, 201, 198, 204, 196, (197), 203	2	2, 1
81	Thallium	Tl	204.39	205, 203	1	1, 3
82	Lead	Pb	207.21	208, 206, 207, 204, (203, 205, 209, 210)	2	2, 4
83	Bismuth	Bi	209.00	209	3	3, (5)
84	Polonium	Po			2	2, (4)
85						
86	Radon	Rn	222		0	0
87						
88	Radium	Ra	226.05		2	2
89	Actinium	Ac			3	3
90	Thorium	Th	232.12	232	4	4
91	Protoactinium	Pa	231		5	5
92	Uranium	U	238.07	238, 235	6	4, 6

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* J. Am. Chem. Soc., **59**, 225 (1937).

† Taken from Table Internationale des Isotopes Stables, Premier Rapport de la Commission des Atomes, 1936.

If no value is given, no search for isotopes has as yet been made, or the data are inconclusive. A single value indicates that a search has been made and no isotopes have been found. Where isotopes are given, an attempt has been made to list them in the order of their abundance, and to denote by parentheses those which may be in doubt.

CHAPTER II

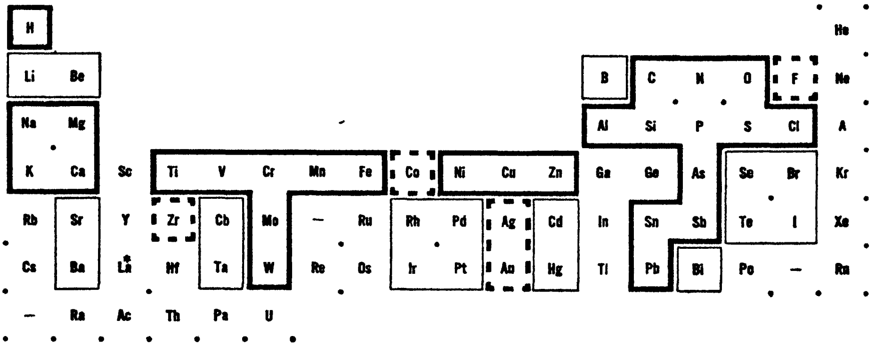
OCCURRENCE OF THE ELEMENTS AND THE CLASSIFICATION OF MATERIALS

A. Occurrence of the Elements

In his analyses of inorganic materials, the analyst can expect to encounter a wide variety of elements. Some he will encounter continually, some quite often, some occasionally, and some very rarely if ever. The relative frequency with which he will encounter the elements is shown in Table 6.

TABLE 6

Determinations Called for in Applied Chemical Analyses



* Also elements 58–71.
Heavy blocks inclose elements that are determined most often.
Broken blocks inclose elements that are determined quite often.
Light blocks inclose elements that are determined occasionally.
Elements not inclosed are determined very seldom.

This refers, of course, to general analytical work rather than work in a special field, such as the gas-mantle industry, in which the chemist's chief problem would be the so-called rare earths, or the platinum industry, in which the chemist's major concern would be determinations of the platinum metals.

The occurrences of the various groups of elements in minerals, rocks, ores, ceramic products, ferrous and non-ferrous materials, and chemical compounds are discussed in detail in the following sections.

B. Composition of Minerals

Minerals are inorganic chemical compounds that occur in nature. Every distinct inorganic chemical compound which occurs in nature and has a definite molecular structure, or system of crystallization and well-defined physical properties, constitutes a mineral species. Approximately one thousand species have been recognized. Only a few of these can be considered as common, and of importance either as rock-forming minerals, as constituents of ores of useful metals, or as otherwise valuable in the arts.

Minerals exhibit all degrees of complexity in composition, and most of the elements appear as a predominating constituent in one or more minerals. To mention a few, we have orthoclase, $KAlSi_3O_8$; gypsum, $CaSO_4 \cdot 2\,H_2O$; thortveitite, $Sc_2O_3 \cdot 2\,SiO_2$; titanite, $CaTiSiO_5$; vanadinite, $3\,Pb_3(VO_4)_2 \cdot PbCl_2$; chromite, $FeCr_2O_4$; rhodochrosite, $MnCO_3$; magnetite, Fe_3O_4; smaltite, $CoAs_2$; millerite, NiS; malachite, $(CuOH)_2CO_3$; calamine, $(ZnOH)_2SiO_3$; argyrodite, $4\,Ag_2S \cdot GeS_2$; scorodite, $FeAsO_4 \cdot 2\,H_2O$; crookesite, $(Cu, Tl, Ag)_2Se$; and bromyrite, $AgBr$.

TABLE 7

Average Composition of the Atmosphere and Known Terrestrial Matter*

	Lithosphere	Hydrosphere	Atmosphere	Average
Oxygen	46.46	85.79	23.024	49.20
Silicon	27.61	......	......	25.67
Aluminum	8.07	......	......	7.50
Iron	5.06	......	......	4.71
Magnesium	2.07	0.14	......	1.93
Calcium	3.64	0.05	......	3.39
Sodium	2.75	1.14	......	2.63
Potassium	2.58	0.04	......	2.40
Hydrogen	0.14	10.67	......	0.87
Titanium	0.62	......	......	0.58
Carbon	0.09	0.002	......	0.08
Chlorine	0.05	2.07	......	0.19
Bromine	......	0.008	......	......
Fluorine	0.03	......	......	0.03
Phosphorus	0.12	......	......	0.11
Sulphur	0.06	0.09	......	0.06
Manganese	0.09	......	......	0.09
Barium	0.04	......	......	0.04
Strontium	0.02	......	......	0.02
Nitrogen	......	......	75.539	0.03
All other elements†	0.50	......	1.437‡	0.47
	100.00	100.00	100.00	100.00

---

* F. W. Clarke, The Data of Geochemistry, U. S. Geol. Survey Bull. 770, pages 36 and 45 (1924).

† As for the "other elements" George von Hevesey (Chemical Analysis by X-rays and Its Applications, McGraw-Hill Book Co., 1932) estimates that the percentages of some of these are as follows: Cr 0.04, Zr 0.03, Ni 0.02, V 0.02, Cu 0.01, and Y 0.01. It is interesting to note that the estimated total percentage, approximately 0.026, of the 19 so-called "rare earths" (21, 39, 57–71, 89, and 90) is considerably in excess of the total percentage, approximately 0.017, of 19 such well-known elements as Pb, Sn, Sb, As, Hg, Bi, Cd, Mo, Ag, Au, Pt, Co, W, U, Be, B, I, Br, and Se.

‡ Practically all argon, but also including small amounts of krypton, xenon, neon, helium, aqueous vapor, hydrogen dioxide, ozone, carbon dioxide, ammonia and other compounds of nitrogen, sometimes sulphur, traces of hydrogen, organic matter, and suspended solids.

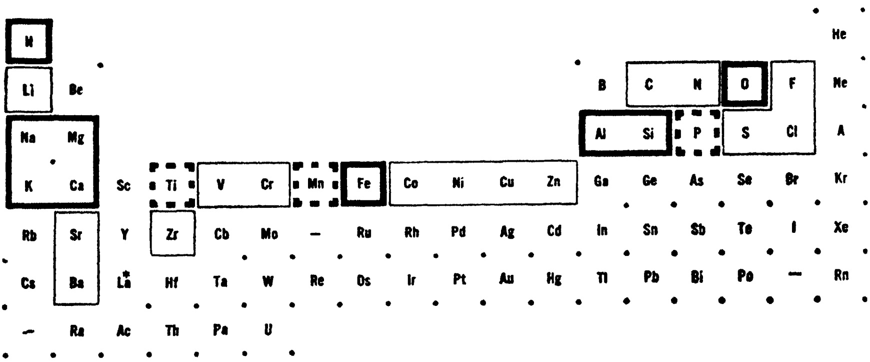
C. Composition of Rocks

Rocks, with the exception of a few glassy lavas, are aggregates of mineral particles. Usually the rock is composed of different minerals (like granite), but sometimes it contains only one (like calcite).

According to Clarke,[1] the known matter of our globe is composed of about 0.03 per cent of atmosphere, 7 per cent of ocean (hydrosphere), and 93 per cent of solid crust (lithosphere). The last refers to the surface layer of the earth, to a depth of 10 miles, consisting of igneous rocks, together with a comparatively small amount of sedimentary rocks (altered igneous material) and decomposition products such as sand, clay, and soil. The atmosphere is composed of nitrogen and oxygen, together with small amounts of the noble and other gases. In the hydrosphere, oxygen and hydrogen (as water), and chlorine and sodium (as salt), predominate, though notable amounts of other elements leached from the surface of the earth are also present. The average composition of the atmosphere and known terrestrial matter is illustrated in Table 7.

TABLE 8

Elements Most Often Encountered in the Chemical Analysis of Rocks


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy blocks inclose major constituents.

Heavy broken blocks inclose common minor constituents.

Light blocks inclose minor constituents that may occur in weighable or easily discoverable quantities.

It will be noted that the lighter elements predominate over the heavier, and that elements of higher atomic weight (55.84) or atomic number (26) than iron are not abundant. The mean density (about 5.5) of the earth, however, is about double that of the rocks at its surface (about 2.8), and so it is likely that heavier substances are concentrated in its interior.

The elements most often encountered in chemical analyses of rocks are shown in Table 8. All occur in the combined state, and not in the metallic or gaseous condition. If a rock should happen to carry appreciable amounts of minerals that contain as essential ingredients any of the minor constituents, these, of course, are also determined.

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[1] F. W. Clarke, The Data of Geochemistry, U. S. Geol. Survey Bull. 770, page 22 (1924).

D. Composition of Ores

Ores are natural concentrations of metalliferous minerals that contain metallic elements in sufficient quantity and purity to warrant their exploitation. Like minerals, they present wide variations in their constituents. Sometimes ore deposits contain the metals themselves, but more often they contain compounds such as sulphides, carbonates, sulphates, or silicates. Deposits may contain more than one metal, or more than one compound of a metal. In addition, they may also contain minerals such as quartz or limestone that are of little or no value. Such material is called gangue.

E. Composition of Ceramic Materials

Ceramic materials exhibit wide differences in the kind and percentages of their constituents. As a rule, all contain the ordinary constituents of rocks, although not in the same order of abundance. In addition, they may contain one or more of other constituents such as lead, copper, cadmium, bismuth, tin, antimony, arsenic, molybdenum, or gold of the Hydrogen Sulphide Group; zirconium, titanium, chromium, or uranium of the Ammonium Hydroxide Group; cobalt, nickel, or zinc of the Ammonium Sulphide Group; and acidic constituents such as boron, phosphorus, sulphur, or fluorine.

F. Composition of Ferrous Materials

Irons and steels always contain Fe, C, Mn, P, S, and Si, together with small amounts of oxygen (as oxides or slags), and of nitrogen (as nitrides). Other elements likely to be present are hydrogen (as hydrides) and more or less Cu, Ni, Cr, V, Mo, As, Sn, Sb, Al, and Ti which have been intentionally added or introduced through raw materials or scrap. Ferroalloys, alloy irons, and alloy steels contain higher percentages of certain of these constituents than plain irons and plain carbon steels and may, in addition, contain other elements such as tungsten, cobalt, zirconium, tantalum, selenium, and boron.

The following compositions of other alloys illustrate combinations of elements that can be expected. Each division embraces numerous alloys in which the percentage compositions of the major constituents vary considerably. Only those constituents that have been intentionally added for alloying purposes in one or more alloys of the type are listed. Elements connected by hyphens are those that occur most often in alloys of the type, but are not necessarily present in all of them. Elements in parentheses are used but seldom. Elements that may occur as impurities are not listed.[2]

Resistance Alloys: Ni-Cr-Fe-Mn-Cu-Zn, Si, Al (C, W, Sn, V, Co).

Heat-resisting Alloys: Ni-Cr-Fe-Si, Mn, C, Cu (Al, W, Mo, Co, V, Zr, Sn).

Stainless and Corrosion-resisting Alloys: Cr-Ni-Fe, Si, C, Mn, W, Cu, Mo (Al, Co, Au, Ag, Ti, Zr, Ta, P, V, B).

Cobalt Alloys, Tools, Corrosion-resisting, Heat-resisting, etc.: Co-Cr-W-Ni-Fe, C, Si, Mo (Mn, V, Ti, Cu, Al, Ag).

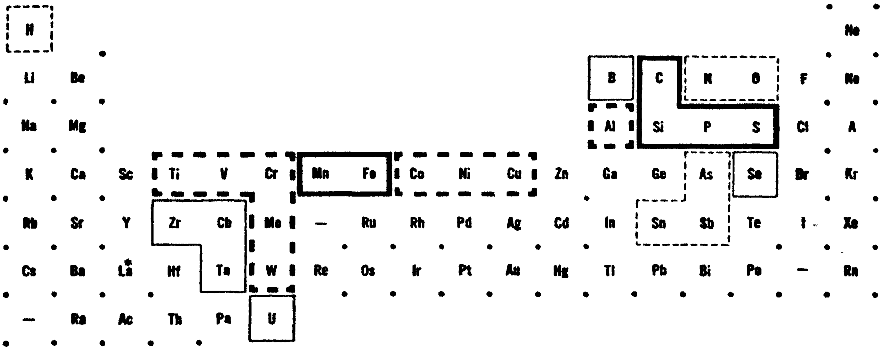
Cutting Tools, Dies, Hard Alloys: W-C-Co, Ni, Cr, Mo, Ti, Si (Al, B, Fe, Zn, Ce).

Pyrophoric Alloys: Fe-Ce, La, Y, Er, Mn, Cr, Ti, Sb, Mg, Al, H.

The elements that are most often encountered in analyses of ferrous materials are shown in Table 9.

TABLE 9

Elements That May Be Encountered in Analyses of Irons, Steels, and Ferroalloys


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy blocks inclose elements common to cast irons and plain carbon steels.
Heavy broken blocks inclose common alloying or scavenging elements.
Light blocks inclose elements occasionally used in special steels.
Light broken blocks inclose elements that usually occur as impurities.

G. Composition of Non-Ferrous Materials

Non-ferrous metals and alloys include a wide variety of materials in which the predominating constituent may be copper, tin, lead, zinc, aluminum, magnesium, silver, gold, platinum, or bismuth, always associated with varying amounts of other elements that are present as alloying constituents or as impurities introduced through raw materials or the use of scrap. The complexity of this field of analysis is illustrated in Table 10, and by the following list of alloys. Each division embraces numerous alloys that may vary considerably in the percentage composition of the major constituents. Only those constituents that have been intentionally added for alloying purposes in one or more alloys of the type are listed. Elements connected by hyphens are those that occur most often in alloys of the type, but are not necessarily present in all of them. Elements inclosed in parentheses are used but seldom. Elements that may occur as impurities are not listed.[3]

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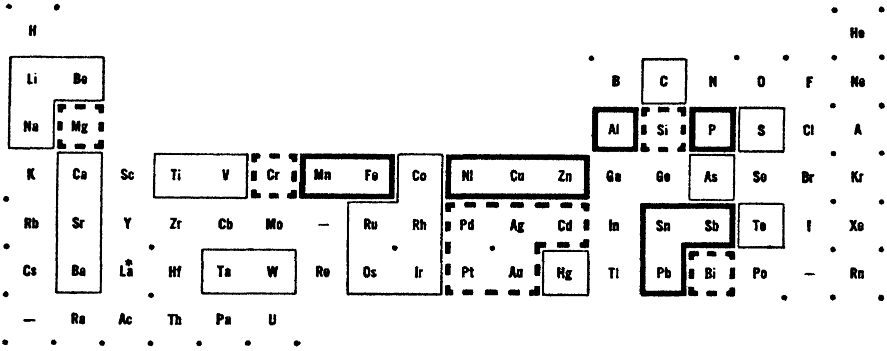
[2] For more detailed information, consult A List of Alloys by W. Campbell, Proc. Am. Soc. Testing Materials, **30** [1], 336 (1930).

TABLE 10

Elements That May Be Encountered in Analyses of Non-ferrous Alloys


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy blocks inclose elements most commonly encountered in analyses of non-ferrous alloys.

Broken blocks inclose elements quite frequently encountered in certain types of non-ferrous alloys.

Light blocks inclose elements occasionally encountered in special alloys.

Hard Coppers: Cu-Cd, Cu-Cd-Sn, Cu-Sn, Cu-Sn-Si, Cu-Si, Cu-Be.

Copper-Nickel Alloys (Monel, Coinage, etc.): Cu-Ni, Mn, Fe, Al, Sn (Si, Zn, W, Bi, Cd).

Copper, Nickel, Zinc Alloys (Argentan, German Silver, etc.): Cu-Ni-Zn-Fe-Sn-Pb, Mn, Al (Bi, Co, Ag, Cd, Sn, P, Cr, W, Sb).

Brasses: Cu-Zn-Sn-Pb-Fe, Mn, Al, Ni (Si, P, As, Sb, V, W, Bi, Au).

Bronzes: Cu-Sn-Zn-Pb-P, Fe, Ni, Sb (Mn, As, Al, Si, Cr, Bi, C, S, Co, W, Pt).

Tin-base Alloys: Sn-Sb-Cu-Pb, Zn, Bi, Al (Fe, Ni, P, Cd, Ag, Ca).

Lead-base Alloys: Pb-Sn-Sb-Cu, Ca, Ba, Cd, Bi (As, Zn, Fe, Na, Ag, Ni, P, Li, Hg, Sr).

Zinc-base Alloys: Zn-Cu-Sn-Sb-Pb, Al, Fe, Cd (Mg, Ag, Bi, Ni, P).

Fusible Metals: Bi-Sn-Pb-Cd (Hg, Sb, Zn).

Gold Alloys: Au-Ag-Cu, Zn, Ni, Pd, Pt, Cd (Fe, Al, W, Mn, Ir, Cr).

Silver Alloys: Ag-Cu-Zn-Sn, Ni, Cd (Mn, Sb, Sn, Au, Pt).

Aluminum Bronzes: Cu-Al-Fe-Zn-Ni-Mn (Si, Sn, Pb, P, Au, Mg, Ti, Co, Cr).

Copper-Manganese Alloys: Cu-Mn-Fe-Zn-Sn-Ni, Al, Pb (Si, C).

Copper-Silicon Alloys: Cu-Si-Ni, Mn, Fe, Sn, Al.

Corrosion-resisting Alloys: Cu-Ni-Fe, Mn, Zn, Sn (Al, Pb, Si, Mo, C, Cr, Co, Sb).

Aluminum Alloys: Al-Cu-Zn-Mn-Mg-Ni-Fe-Si, Sn (Cr, Pb, Ag, Sb, Cd, W, P, Bi, Ti, Ca, Co, Au, V, Li).

Magnesium Alloys: Mg-Al-Mn-Zn, Cu, Cd.

Platinum Alloys: Pt-Au-Ag, Cu, Pd, Ni, Ir (Zn, Rh, Ru, Os, Co, Cd, Ag, Sn, As, V).

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[3] For more detailed information consult A List of Alloys by W. Campbell, Proc. Am. Soc. Testing Materials, **30** [1], 336 (1930).

In addition to the above, certain other alloys such as beryllium-aluminum and tantalum alloys have found use.

H. Composition of Chemical Compounds

Chemical compounds, like ores and minerals, exhibit all degrees of complexity. However, outside of student analyses or researches on newly prepared compounds, the major constituents are rarely determined, and tests are confined to those of undesirable impurities. Such tests usually involve determinations of constituents that occur in very small amounts, and constitute a special field in analytical chemistry, the testing of chemical reagents. This will not be covered in this discussion except by calling attention to the great importance of testing analytical reagents to see whether they are sufficiently pure for the work in hand.

I. Classification of Materials

In general, visual inspection suffices for the classification of inorganic materials into definite classes, such as metal, mineral, rock, ceramic material, or chemical compound. As a rule, visual inspection also enables the analyst to assign metallic samples to definite classes such as ferrous (iron a predominating constituent) or non-ferrous (iron absent or a minor constituent). As regards the latter, it is usually possible to assign the type, as for example brass, bearing metal, or light aluminum alloy.

Once a metal has been assigned to a definite class, the presence of certain constituents is taken for granted, and quite often the major constituent is reported by difference, if at all. Thus it is certain that plain cast iron or steel will contain carbon, manganese, phosphorus, sulphur, silicon, and small amounts (each usually under 0.1 per cent) of elements such as copper, nickel, chromium, vanadium, molybdenum, arsenic, and tin. Similarly, there is no need to test brasses qualitatively for copper and zinc or, for that matter, for elements such as lead and iron.

The identification of the commoner minerals is a specialized branch of chemical analysis in that it deals with definite species. For a large number of minerals, the mineralogist does not need to give much more thought to the identification than an ordinary mortal does in deciding whether a vegetable is a cabbage or a carrot. In other words, he does not need to make any tests at all to make sure of the identity of minerals such as pyrite (iron sulphide, FeS_2), galena (lead sulphide, PbS), cinnabar (mercuric sulphide, HgS), or sphalerite (zinc sulphide, ZnS). In cases of doubt, easily determined characteristics usually suffice, such as color, specific gravity, hardness, crystal form, solubility in acids, behavior before the blowpipe, and the character of the streak which the mineral gives when rubbed across unglazed porcelain. A reasonably comprehensive outline of determinative mineralogy is beyond the scope of this book. The composition of each mineral was, of course, originally determined by qualitative and quantitative methods of chemical analysis.

There is small need for qualitative testing of rocks, for the analyst usually knows what elements to expect. If there is reason to suspect something out of the ordinary, such as the presence of significant amounts of barium, a quantitative method is chosen that will reveal the suspected element, or else tests are made at the point where the element should be caught in the usual analysis, as for example strontium in the oxalate precipitate obtained in the determination of calcium, or lithium in the chlorides obtained in the determination of sodium.

The problem of classifying ceramic materials presents different degrees of complexity. As for glasses, by far the greater number are of the soda-lime type in which the analyst knows that he is dealing with SiO_2, Na_2O, CaO, more or less MgO and Al_2O_3, and small amounts of Fe_2O_3, SO_3, As_2O_3, and Cl. Glasses of other types are betrayed by physical characteristics such as density or opacity, by preliminary tests for suspected elements, or by examination of precipitates obtained during the course of the analysis.

Chemical compounds present the greatest diversity of composition, and an unknown material (for example, BN) may call into play all the resources of the analyst.

CHAPTER III

SAMPLING

In a chemical analysis, the first consideration is the use of a sample that truly represents the material under test. The procuring of such a sample is always an important part of the analysis. Sometimes it requires more time and effort than the analysis itself. The steps that must be followed in taking a sample vary with different materials, and may include: (1) taking the laboratory sample; (2) taking the test sample; and (3) treating the test sample before weighing.

In taking the laboratory sample of material such as lump ore, the analyst can see at once that great care must be exercised if the sample is to be truly representative. On the other hand, there is often no warning that care is needed. A piece of metal may appear to be perfectly uniform in structure, and yet contain areas in which certain constituents are segregated to such an extent that entirely misleading results are obtained if samples are taken from them. This is illustrated in Table 11. Even if the material is uniform in structure, different-sized particles obtained by crushing or machining may differ in composition, because some of the constituents are more brittle than others and thus concentrate in the finer portions. This is illustrated in Table 12. In ores containing gold nuggets the gangue is the brittle constituent and the flattened nuggets are concentrated in the coarser portions.

Aside from the difficulties that have been mentioned, the reduction of large particles may also lead to chemical changes in the particles, as for example the partial oxidation that results when materials such as pyrite or refined silicon are ground to a fine powder, or the fixation of water and carbon dioxide that accompanies fine grinding of oxidized materials such as soda-lime glass.

Descriptions, or even outlines, of methods for the sampling of different types of materials would require too much space to be covered in this book. The purpose of introducing the subject is to draw attention to the necessity for a very careful consideration of the method by which the laboratory sample is taken.

The difficulties in the way of obtaining a representative sample for analysis do not always stop with the taking of the laboratory sample. If the latter is not perfectly homogeneous, the operation of taking the smaller sample that is actually used in the analysis may be even more important and difficult than that of taking the laboratory sample. This operation

TABLE 11

Segregation in a Steel Ingot[1]

(Ingot sawed in half lengthwise and samples drilled as shown)

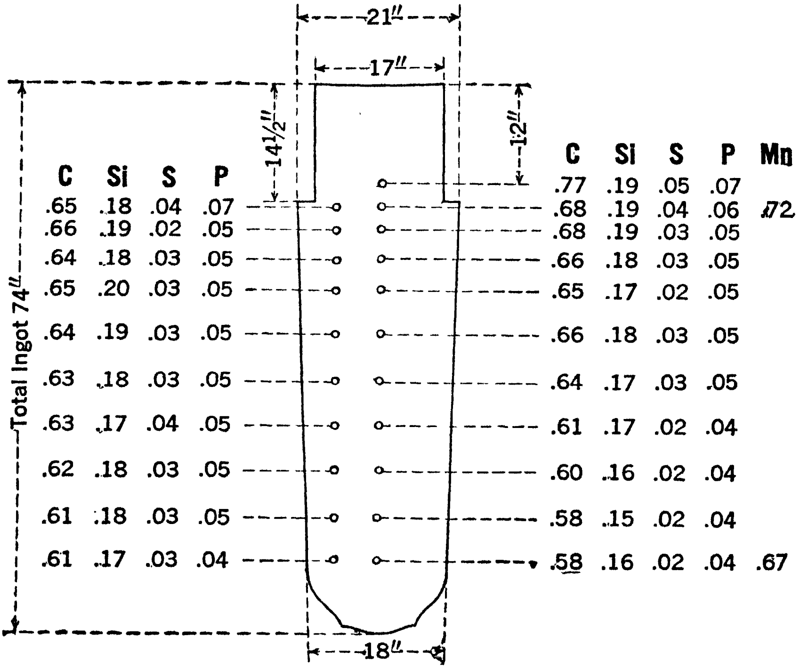

TABLE 12

Differences between the Compositions of Particles in a Sample[2]

Material	Sieve Size	Constituent Determined		
		Carbon		
Cast Iron*	14 - 20	2.45		
	20 - 30	2.27		
	30 - 40	2.04		
		Copper	Lead	Tin
Journal Bearing	14 - 20	70.0	24.4	4.9
	20 - 30	70.2	24.1	4.9
	30 - 80	67.6	27.9	4.7
	> 80	63.2	31.2	4.4
		Tungsten		
Ferrotungsten	80 - 100	77.6		
	100 - 200	80.2		
	200 - 325	79.5		
	> 325	70.4		

* *Free* graphite removed before sifting.

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[1] J. R. Freeman, R. L. Dowdell, and W. J. Berry, Tech. Paper Bur. Standards, No. 363, page 337.

[2] J. A. Scherrer and G. E. F. Lundell, B. S. J. Research 5, 891 (1930).

might appropriately be called sampling the sample. To mention but two in this category, great care must be exercised in selecting a true test sample from the mixture of iron and graphite particles that is obtained when cast iron is machined, and in taking a test sample from the millings of the journal bearing described in Table 12.

The kind of treatment that the test sample should receive before it is weighed depends on the nature of the material. Some samples, such as of igneous rocks, require no treatment at all, for hygroscopic as well as chemically combined water is determined in their analysis. With most materials containing hygroscopic water it is customary to dry the sample at 105–110°C before it is weighed, or else to weigh the sample " as is," and afterward correct results to the " dry basis " as calculated from a determination of moisture carried along at the same time on a separate sample. Drying at 105–110°C may drive off more or less chemically combined water as well as hygroscopic water. In such cases it is often necessary to dry at higher temperatures in order to obtain a sample of definite composition. Finally, samples of certain fired materials, such as powdered soda-lime glass, must be heated as high as 1000°C in order to drive off the water and carbon dioxide which have been absorbed and fixed during grinding, sieving, and storage.

It is obvious that, if the material is markedly hygroscopic, the test sample must receive special protection from the moisture of the air until it has been weighed.

It is also evident that impurities introduced during sampling, such as oil on chips of steel, must be removed at some time or other before the test sample is weighed.

Finally, it should be borne in mind that a sample may gradually deteriorate in storage as a result of chemical changes. These can be illustrated by the slow fixation of water and carbon dioxide by finely ground samples of glass, the oxidation of sphalerite followed by hydration of the zinc sulphate that is thus formed, and the chemical changes and contamination that result when dolomite is stored in tin-lined cans.

CHAPTER IV

PREPARATION OF THE SOLUTION FOR ANALYSIS

A. Solution of the Sample

If quantitative analyses are to be made by usual procedures, the first consideration is to get the weighed test sample into solution. Outside of certain chemicals, very few materials dissolve in water; consequently more rigorous treatments are required. Many substances dissolve in mineral acids, used singly as in the solution of iron ore in hydrochloric acid, or in combination as in the solution of gold in a mixture of nitric and hydrochloric acids.

Quite often, it happens that more or less insoluble matter remains after treatment with acids. If this consists of unattacked material, the solution is carefully filtered, and the washed residue is broken up by igniting, fusing with a suitable flux, and dissolving the cooled melt in water or acid. As a rule, the solution so obtained is added to the original solution, although sometimes the examination of the solution of the melt is carried along separately.

Sometimes decomposition of the material by acid is complete, and yet a residue remains, as when bronze is dissolved in diluted nitric acid (1 + 1), or a tungsten steel is dissolved in hydrochloric and nitric acids. Such reactions are useful in both qualitative and quantitative tests. With bronze, the formation of the residue (white metastannic acid) serves as an indication of the presence of tin and also for the separation of the tin from most of the other constituents of the bronze. With tungsten steel, the residue (yellow tungstic acid) serves for the detection of tungsten and also for the separation of tungsten from most of the other constituents of the steel.

Some materials are so insoluble that a wet attack is useless. These must be broken up by fusing with fluxes such as sodium carbonate, sodium peroxide, borax, or potassium pyrosulphate. A flux that will accomplish the desired object must be chosen, and the fusion must be made in a container that will not be seriously attacked or cause undesirable contamination.

B. Solvents or Fluxes for Various Materials

In Table 13, the solvents or fluxes for general purposes follow immediately after the name of the substance. No concentration is designated for acids unless a particular concentration is decidedly preferable. Following the general solvents are reagents and specific concentrations of acids that may

TABLE 13

Solvents or Fluxes for Various Materials

Ores and Refractories

Alkalies in most ores, minerals, and refractories	Fusion with $CaCO_3 \times NH_4Cl$	Limestone	1, 6
Al_2O_3 (alundum, mullite, etc.)	(6 × 12), 6	Manganese ores (MnO_2)	1, (2 + H_2O_2); for Mn(2c + H_2O_2) −
Bauxite	(2 × 3 × 5) −, (6 × 12), 6, 7, 10	Monazite sand	3a, (NaF × 10) + 1g
Chromium ores	7, (3 × 4), (6 × 12); for Cr 7; for SiO_2, Fe, Al, CaO, and MgO (3e × 4) −	Phosphate rock	(1 × 2) −, 1 −, 2 −
Feldspar	(5 × 3), (1 × 5 × 4), 6	Refractories (high Al)	(6 × 12), 6, 7, 10, (5 × 2 × 3) −
Fluorspar	3, 4, 8, 6, 9	Silica sand	5, (1 × 5), (2 × 5), 6
Iron ores	1, (1 × 2); for Fe, Si, P, Al, Ca and Mg, 1 or (1 + 2) or (1 + 2) + 6; for Mn (1 × 5 × 3b); for S 2a; for Cr 7	Silicon carbide	8
		Slags	1 −, 4 −, (1 × 2) −, 7, (6 × 12)

Minerals

Beryllium	6, (6 × 12)	Mercury	Ignition with CaO or Fe yields Hg
Boron	1 −, 6, Fusion with 2 Na_2HPO_4 × 1 HPO_3	Molybdenum	1 −, 3 −, (1 × 2), 7, 9, 8
Cadmium	1 −, (1 + 2) −, 2 −	Nickel	[(2 + 1) −] + 6 or 10
Chromium	7 −, 8 −	Rare earths	Fusion with KHF_2, 1 −, 3a, 10, 6, 7
Cobalt	(1 + 2) −, (2 + 3) −, 7	Selenium and tellurium	7, 8
Columbium	2 × 5 −, 9, 7, 10, SCl_2, or SCl, fusion with KHF_2	Silver	(2 −) + 6
Copper	1 −, (1 + 2) −, 5 −, 6, 10	Sulphur	7, 8, 2a + Br_2
Fluorine	3 −, 4 −, 6, (6 × SiO_2), 9, 8	Tantalum	See Cb
Germanium	(6 × S) −, 11, 1 × 3 × 4 × 5	Thallium	3a, (1 + 2 + 3)
Lead silicate	6	Thorium	(1 −) + 10, 3a, (NaF × 10) + 1g
Lead sulphide	1 + 2	Tin	7, 9, (2 −) + 7 or 9 (cassiterite, fusion with 6 + K_2CO_3 + S)
Magnesium	1 −, 6, or (1 −) + 6		
Manganese	1 −, (1 × 3), (1 × 3 × 5), 6, 10		

TABLE 13 — *Continued*

Minerals

Titanium	5, (5 × 2 × 3), 9, (9 × 6), (9 × 7), 10−, fusion with KHF_2	Vanadium	(1 + 2)−, [(1 + 2) −] + 5, 6, 7, 10
Tungsten	(1 + 2)−, 6, 7, 10	Zinc	Same as cadmium
Uranium (pitchblende, etc.)	2−, (2 + 1)−, (1 × 5), 10	Zirconium	12, 7, 10, fusion with KHF_2, (8−) + 10 + 3g

Metals

Alkali metals (Li, Na, K, Rb, Cs)	H_2O	Magnesium	2, 1, 3
Alkaline earth metals (Ca, Sr, Ba)	1, 2, H_2O	Manganese	2, (2 + 5), 1, 3
Aluminum	1, 3, 11, 2*	Mercury	2b, 3a
Antimony	(1 × 2), (1 × Br_2), 2	Molybdenum	2, (1 × 2), 3a, 7
Arsenic	(1 × 2), 3a, 2	Nickel	2, 1, 3
Beryllium	1, 3, 11	Osmium	Alkaline oxidizing fusion
Bismuth	2, 3a, 1*	Palladium	(1 × 2), 2*, 10
Boron	2, 3, 9	Platinum	(1 × 2), Halide solutions containing oxidizing agents
Cadmium	2, 1, 3	Rhenium	2, 3*
Cerium and other rare earths	1, 2, 3, H_2O*	Rhodium	Alkaline oxidizing fusion: NaCl + Cl_2
Chromium	1, 3, 5	Ruthenium	Alkaline oxidizing fusion
Cobalt	2, 1, 3	Selenium	(1 × 2), 2, 3a
Columbium	(2 × 5), 9, 5*	Silicon	(2 × 5), 9, 6, 11*
Copper	2, 3a	Silver	2, 3
Gallium	(1 × 2), 1, 11, 2, 3	Tantalum	(2 × 5), 9, 5*, 3a*
Germanium	3a, 2, 9	Tellurium	2, (1 × 2), 3a
Gold	(1 × 2), KCN, (3a + 2)*, Halide solutions containing oxidizing agents	Thallium	2, 3, 1*
		Thorium	1a, (1 × 2), 3*, 5*
		Tin	1a, (1 × 2), 3a, 2b−
		Titanium	5, 1, 2, 3
Hafnium	Same as Zr	Tungsten	(2 × 5), 9*, 7*, 10*
Indium	2, 1, 3	Uranium	1, 3, 2, H_2O*
Iridium	Alkaline oxidizing fusion	Vanadium	2a, 3a, 5, 7, 9
		Zinc	2, 1, 3, 11
Iron	1, 2, 3, 4, 5	Zirconium	5, (1 × 2), 3a, 1*
Lead	2		

Ferrous Metals

Plain steels and cast irons	**1, 2, 3, 4, 5; for Mn, P, As 2c or 2d; for S 2a**	**High-speed steels**	**(1, 3, 4, or 5) +2; for Mn 3g, or (3g + 2g) or 2b;**

TABLE 13 — *Continued*

Ferrous Metals

High-speed steels — *Continued*	for P (2d + 1); for S 2a or (2a + 1 or 5); for Si (1a × 2a) + 3b, or (1a × 2a) + 4a	Fe-V	2d−, (2d × 3), (2d + 5) or 7; for P (2d + 5); for S 2a; for Si (2b × 3b) or 7; for As, 7
Stainless steel	(1 or 3) + (2 or 5); for P (2b + 5); for S (2a + 1)	Fe-Mo $CaMoO_4$	2d, 2d + 5, 6 × 7 [(1h + 3b)−] + 6 + 3g
Spiegeleisen, Fe-Mn and Mn metal	2−, 2 + 5, 3−, or 1 + 2; for S 2a; for Si 2d + 3a; for P (2a + 1)−; for As (2d + 3b); for Cr and V (3g−) + 6 + 3g, or 7	Fe-W Fe-Co Fe-Ti	7, (2 × 5); for Si, S, Sn, Sb, As, 7 2 3d−, (3b × 1a × 2a), 7, 8, or 10; for Ti [(3b × 1a × 2a)−] + 10 + 3b; for Mn (2b + 5) or (3d + 2a + 1a); for P and S 8; for Al, 9
Ferrophosphorus	7, 3a, 4a, (2 × 5); for S and Si, 7		
Fe-Si and refined Si	7, 8, 9, (2 × 5); for Si 7, 8 or 9; for S, P, As (2a + 5)	Fe-Zr	(3b + 5a + 2a), 7; for Si, P, S, and Sn, 7
Fe-Cr or Cr-metal	7, 1a−, 3e−, 5−, or (3e × 5); for Si 7 or 3e; for P and S 7, 2d−	Fe-Ta	2 × 5, 7; for S (2a + 5), or 7; for Si, 7
		Fe-B	2, 7; for B, 7

Non-ferrous Metals

Aluminum and aluminum-base alloys	1, 3, 2−, (2 × 3); for Si, Fe, Cd, Cr, V, and Mo (3d × 1 × 2)−; for Mn (3h + 2); for Cu, Ni, Zn, and Pb [(11−) + 2b]; for Ca and Mg [(11−) + 1b]; for Ti [(11−) + 10 + 3g]; for U [(11−) + 3b]	Lead and lead-base alloys Magnesium and magnesium-base alloys Nickel-chromium alloys	(1 × 2), 2−, 3a−; for Sn, Sb, and As 3a−; for Pb (2 × tartaric acid); for Fe, Cu, and Bi (1 × 2) 3−; for Mn, Si, Fe, and Ni (3e + 2) (1 × 2), 3, (3 × 2), (4 × 2)
Copper, brasses, and bronzes	(1 × 2), 2−; for Sn, Sb, Pb, Cu, Zn, Fe, Al, and Ni 2b−; for As and S 2a−; for P (1a × 2a)	Tin and tin-base alloys Zinc and zinc-base alloys	2−, 3−; for Sn or Sb (3a + 1) or 2b−; for Bi, Cu, Fe, and Pb (1 × 2) 1, 2, 3−; for As and P 2b

* Denotes slow attack.

be used for specific purposes. More detailed information is contained in the following key:

KEY

1 = HCl
2 = HNO_3
3 = H_2SO_4
4 = $HClO_4$
5 = HF
6 = Na_2CO_3 fusion
7 = Na_2O_2 fusion

8 = $Na_2CO_3 \times KNO_3$ fusion
9 = $NaOH$ or KOH fusion
10 = $K_2S_2O_7$ fusion
11 = $NaOH$ or KOH solution
12 = $Na_2B_4O_7$ fusion

a = concentrated acid
b = 1 + 1 acid
c = 1 + 2 acid
d = 1 + 3 acid
e = 1 + 4 acid
g = 1 + 9 acid
h = 2 + 1 acid

(+) connecting two numbers means that it is preferable to add the second reagent in small portions to the first as the reaction proceeds, or after the first has completed its action. If the second reagent happens to be a flux, it means that the residue left after the first treatment is ignited and fused with the flux as designated.

(×) connecting two or more numbers means that the substances so joined are used in the form of a mixture added all at once.

(−) following a number or group of numbers means that a residue may remain after the treatment. If the analyst fears that this may contain some of the constituents to be determined, it must be decomposed, as by filtering, igniting, and fusing with an appropriate flux. In some cases the residue may contain none of the element sought by the analyst; in others it may contain all of it.

For example, $[(1h + 3b) -] + 6 + 3g$ after $CaMoO_4$ designates the usual procedure for dissolving this material, and indicates that treatment with $HCl(2 + 1)$ followed by treatment with $H_2SO_4(1 + 1)$ is likely to leave a residue. This residue must be filtered off, ignited, and fused with Na_2CO_3. The melt is taken up in H_2SO_4 (1 + 9).

HCl (2 + 1) means 2 volumes of HCl (sp gr 1.18) diluted with 1 volume of H_2O. This system of designating diluted acids is used throughout this book. If no dilution is specified, the concentrated reagent is meant.

It is to be noted that silica (and boron) will be lost in treatments in which hydrofluoric acid or fluorides are used.

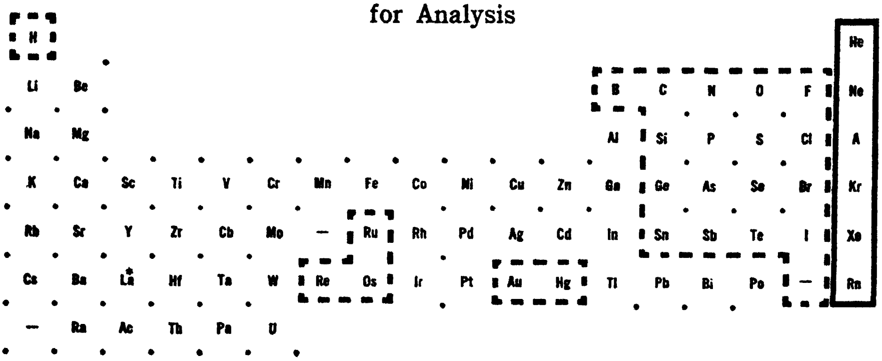
C. Elements That May Volatilize During the Preparation of the Solution for Analysis

In preparing solutions of materials to be analyzed the analyst must, of course, make sure that none of a constituent to be determined is lost. Chief among the causes of such losses is volatilization. Elements that may volatilize during the preparation of solutions are shown in Table 14. Of these, it is obvious that gases such as hydrogen, oxygen, nitrogen, chlorine, carbon dioxide, hydrogen sulphide, hydrogen selenide, hydrogen telluride, and the noble gases will be driven off if solutions are boiled, or even if the concentration exceeds that which the solution can hold at lower temperatures. The gases lost in this way include those that occur as such, or that may be formed as the result of reactions, as for example those of carbonates, sulphides, phosphides, arsenides, antimonides, selenides, tellurides, or peroxides with acid, or of silica or boric acid with hydrofluoric acid.

Other compounds that may be lost are the volatile acids, the volatile oxides, and the volatile compounds formed by the action of acids. Chief among the last are chlorides such as the tetrachloride of germanium and the trichloride of arsenic which can be completely volatilized from boiling hydrochloric acid solutions, and the trichloride of antimony, the tetrachloride of tin, the dichloride of mercury, and the oxychlorides of selenium and tellurium, which volatilize to some extent from hydrochloric acid solution unless special precautions are used. The volatile acids include boric, nitric, and the halogen acids which volatilize from boiling aqueous solutions, and phosphoric acid which volatilizes from boiling concentrated sulphuric or perchloric acid. The volatile oxides are the heptoxide of rhenium and the tetroxides of osmium and ruthenium. The last two volatilize from boiling nitric acid or nitric acid together with either perchloric or sulphuric acid. Rhenium volatilizes from fuming (200°C or higher) perchloric or sulphuric acids, either alone, in combination with each other, or after mixing with hydrochloric or nitric acid. Rhenium does not volatilize from boiling solutions containing only hydrochloric acid, nitric acid, or aqua regia. Gold is volatilized to some extent if solutions containing aqua regia are rapidly evaporated to dryness, or if such solutions are treated with sulphuric acid and evaporated to copious fumes.

TABLE 14

Elements That May Volatilize During the Preparation of Solutions for Analysis


H
He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks inclose elements that are entirely lost.
Heavy broken blocks inclose elements that may be lost entirely or in part.

Just as constituents may be lost during treatments of solutions, so may losses occur during fusions, particularly acid fusions. With the exception of gases, very few substances are lost from alkaline melts, the losses being confined to mercury, certain carbon and nitrogen compounds, and, under exceptional conditions, boron and fluorine. Losses from acid melts result from the same general conditions that cause losses when acid solutions are evaporated.

PART II. METHODS FOR SEPARATING THE ELEMENTS

I. GENERAL PROCEDURE FOR SEPARATING THE ELEMENTS

CHAPTER V

INTRODUCTION

The oldest scheme of analysis, and possibly the one that comes nearest to being in universal use, is that employed in the analysis of the rocks comprising the earth's crust. The reason for this is, of course, that the composition of rocks is limited to varying percentages of a comparatively few elements (see Table 8, page 15), and long-continued practice by thousands of analysts throughout the world has resulted in the development of what might be called a General Procedure for the analysis of rocks and material of similar composition.

In this scheme, the first step is to decompose the material so that the elements[1] can be separated from one another. It is seldom that rocks can be completely decomposed by a wet attack, that is by treating with water or acids other than hydrofluoric. If any considerable amount of the sample, as for example a carbonate rock, can be decomposed by such treatments, it is customary to dissolve as much as possible in diluted hydrochloric acid and then to filter, wash the residue and paper thoroughly, and combine the filtrate and washings with a solution of the residue. This is obtained by fusing the residue with a suitable flux, such as sodium carbonate, after which the melt is cooled and dissolved in hydrochloric acid.

When the sample has been decomposed, the next problem is the separation of its constituents. No attempt is made to isolate one element at a time. Rather, groups of elements that exhibit a common reaction are first separated, as in qualitative analyses, and then the groups are examined for the members that may be present, and their amounts are determined by suitable methods. The elements that are separated fall in six groups: the Acid, the Hydrogen Sulphide, the Ammonium Hydroxide, the Ammonium Sulphide, the Ammonium Oxalate, and the Ammonium Phosphate. These are obtained by the following treatments: (1) evaporation to dryness with hydrochloric acid followed by digestion of the residue in hydrochloric acid and water; (2) treatment with hydrogen sulphide in diluted hydrochloric acid solution; (3) precipitation with ammonium hydroxide after expulsion of hydrogen sulphide and oxidation of reduced elements; (4) precipitation with ammonium sulphide; (5) precipitation with ammonium oxalate; and (6) precipitation with diammonium phosphate. Each treatment is, of course, followed by filtration in order to obtain the group concerned.

---

[1] The term "element" is used throughout this book in the broad sense, which includes the form (atom, ion, molecule, or compound) in which it occurs at the moment.

The treatments do not always yield perfect separations of the groups, and the behavior of certain elements in a given treatment depends on the character and the amount of the other elements that are present. Some elements, notably the alkalies, are not caught in any of the six groups, and must be separated by other procedures. The procedure almost universally followed for the separation of the alkalies is that known as the J. Lawrence Smith method. For this reason, as well as the fact that the separation and determination of the alkalies are usually called for in analyses of materials best covered by the General Procedure, the method is included in the separations that are covered in the detailed discussion of the General Procedure.

CHAPTER VI

DISTRIBUTION OF THE ELEMENTS IN THE GENERAL PROCEDURE

The group in which all or most of a given constituent of a rock may be expected if the treatments are applied in the regular sequence is shown in Table 15. The problem is not always so simple as this compilation might indicate. Very often, as shown in Table 16, the constituents of the material under analysis differ from those of rocks in kind or amount. The distribution of all the elements in the General Procedure is shown in Tables 17 and 18 and, in greater detail, in Tables 19 to 27.

The reactions indicated for radium, actinium, protoactinium, polonium, also the elements that have not been isolated as yet, and most of the elements 58–71 are those that are described in the literature, or inferred from their relationship in the periodic arrangement of the elements. The reactions set down for the others are based on the experiences of the authors, supplemented by extensive tests in which 100-ml portions of solutions containing 10–25 mg of the element in question were tested under the conditions set forth. Unless otherwise specified, the compounds chosen were those in which the element was present in the "most stable valence" shown in Table 5.

It should be remembered that preliminary treatments of a solution may have a marked bearing on the results obtained, as for example those involving changes in valence, or the formation of complex ions such as the ammines that are obtained when solutions of the platinum metals are treated with an excess of ammonium hydroxide.

As stated at the outset, the General Procedure was designed primarily for analyses of rocks, or of oxidized materials of approximately the same composition. For metals, or materials containing significant amounts of elements, such as vanadium, that are not adequately taken care of in the separations, other methods of analysis are chosen. Even so, the order of treatments in the General Procedure is very often followed, if only to obtain a general idea as to the composition of the material under test.

Any change in the order of a treatment is usually accompanied by a marked change in the result obtained. This may, in turn, be radically altered by a slight modification of the treatment itself. These differences in behavior are extremely important, and must be thoroughly understood before the order is changed or a treatment is omitted. For this reason the following chapters will be devoted to descriptions of the results that can be expected if the six treatments are applied: (1) in their regular order; (2) without prior treatments; and (3) in commonly used modifications.

TABLE 15

Distribution of the Constituents of Rocks in the General Procedure

Constituents of Rocks	Group						Constituents Not Caught in the Six Groups
	Acid	Hydrogen Sulphide	Ammonium Hydroxide	Ammonium Sulphide	Ammonium Oxalate	Ammonium Phosphate	
Major constituents	Si	None	Al, Fe	None	Ca	Mg	Na, K, H, O
Common minor constituents	None	None	Ti, P*	Mn	None	None	None
Minor constituents that may occur in weighable or easily discoverable quantities	None	Cu	Zr, Cr, V*	Co, Ni, Zn	Sr	Ba	Li, C, N, S, Cl, F
Constituents that occur but seldom or in very minute amounts	Ta, Cb, W	Mo, Sn, Pt, Ag, Pb, Au	Be, Th, U, Rare Earths	None	None	None	B, He

* Group in which element is usually found.

TABLE 16

Occurrence of the Members of the Groups of the General Procedure in Typical Materials

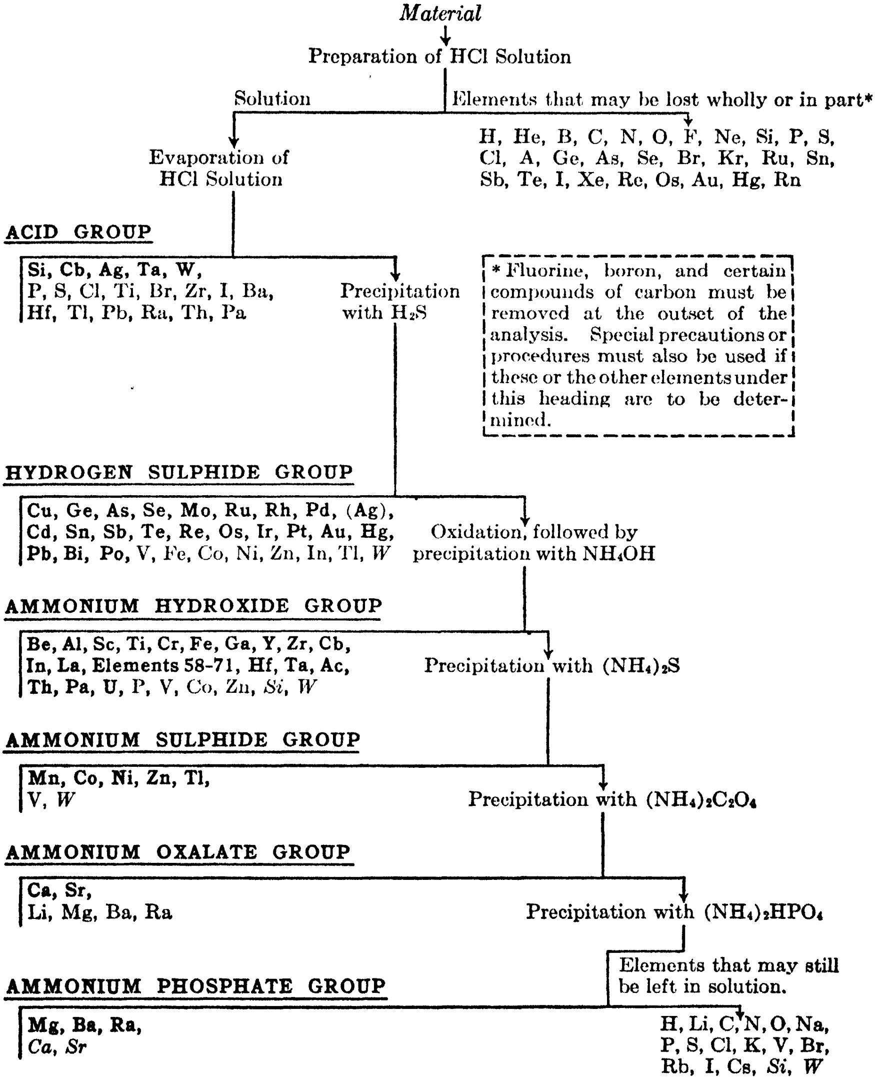
Material	Group						
	Acid	Hydrogen Sulphide	Ammonium Hydroxide	Ammonium Sulphide	Ammonium Oxalate	Ammonium Phosphate	Alkalies (Na and K)
Rocks	1	4	1	3	1	1	1
Ceramic	1	2	1	2	1	1	1
Ferrous	2	2	1	1	4	4	4
Non-ferrous	2	1	2	2	4	2	4
Minerals, Ores, and Chemicals	Depends on the nature of the material.						

1. Common occurrence.
2. May occur in amounts ranging from very small to appreciable.
3. Occur in small amount if at all.
4. Uncommon occurrence.

TABLE 17

Distribution of the Elements in the General Procedure

(ELEMENTS IN EACH GROUP OR SUB-GROUP ARE LISTED IN THE ORDER OF THEIR ATOMIC NUMBERS)



Material

Preparation of HCl Solution

Solution

Elements that may be lost wholly or in part*

H, He, B, C, N, O, F, Ne, Si, P, S, Cl, A, Ge, As, Se, Br, Kr, Ru, Sn, Sb, Te, I, Xe, Re, Os, Au, Hg, Rn

Evaporation of HCl Solution

ACID GROUP

Si, Cb, Ag, Ta, W,
P, S, Cl, Ti, Br, Zr, I, Ba,
Hf, Tl, Pb, Ra, Th, Pa

Precipitation with H_2S

* Fluorine, boron, and certain compounds of carbon must be removed at the outset of the analysis. Special precautions or procedures must also be used if these or the other elements under this heading are to be determined.

HYDROGEN SULPHIDE GROUP

Cu, Ge, As, Se, Mo, Ru, Rh, Pd, (**Ag**),
Cd, Sn, Sb, Te, Re, Os, Ir, Pt, Au, Hg,
Pb, Bi, Po, V, Fe, Co, Ni, Zn, In, Tl, *W*

Oxidation, followed by precipitation with NH_4OH

AMMONIUM HYDROXIDE GROUP

Be, Al, Sc, Ti, Cr, Fe, Ga, Y, Zr, Cb,
In, La, Elements 58-71, Hf, Ta, Ac,
Th, Pa, U, P, V, Co, Zn, *Si*, *W*

Precipitation with $(NH_4)_2S$

AMMONIUM SULPHIDE GROUP

Mn, Co, Ni, Zn, Tl,
V, *W*

Precipitation with $(NH_4)_2C_2O_4$

AMMONIUM OXALATE GROUP

Ca, Sr,
Li, Mg, Ba, Ra

Precipitation with $(NH_4)_2HPO_4$

Elements that may still be left in solution.

AMMONIUM PHOSPHATE GROUP

Mg, Ba, Ra,
Ca, Sr

H, Li, C, N, O, Na,
P, S, Cl, K, V, Br,
Rb, I, Cs, *Si*, *W*

Heavy Type.	**Elements that are precipitated (completely or in large part) when occurring alone.**
Light Type.	Elements that may be found in the group (wholly or in part) although not precipitated when occurring alone and in moderate amount.
Italics.	*Elements that may be found in the group (in small part) through incomplete precipitation in their own groups.*

TABLE 18

Behavior of the Elements in the General Procedure

(The significance of the numbers is as follows: 0 = elements that may be lost entirely or in part during the solution of the sample and evaporation with hydrochloric acid; 1 = Acid Group; 2 = H_2S Group; 3 = NH_4OH Group; 4 = $(NH_4)_2S$ Group; 5 = $(NH_4)_2C_2O_4$ Group; and 6 = $(NH_4)_3PO_4$ Group.)

H (0)																	0 He
Li (5)	3 Be											B (0)(1)(3)	C (0)	N (0)	O (0)	F (0)(1)(3)	0 Ne
Na	6 Mg (5)											3 Al	1 Si (0)(3)	P (0)(1)(3)	S (0)(1)(3)	Cl (0)(1)	0 A
K	5 Ca (6)	3 Sc	3 Ti (1)	V (2)(3)(4)	3 Cr	4 Mn	3 Fe (2)	4 Co (3)	4 Ni	2 Cu	4 Zn (2)(3)	3 Ga	0 Ge (2)	2 As (0)	2 Se (0)	Br (0)(1)	0 Kr
Rb	5 Sr (6)	3 Y	3 Zr (1)	1 Cb (3)	2 Mo	—	2 Ru (0)	2 Rh	2 Pd	1 Ag (2)	2 Cd	3 In (2)	2 Sn (0)	2 Sb (0)	2 Te (0)	I (0)(1)	0 Xe
Cs	6 Ba (1)(5)	3* La	3 Hf (1)	1 Ta (3)	1 W (2)(3)	2 Re	2 Os (0)	2 Ir	2 Pt	2 Au	2 Hg (0)	4 Tl (2)	2 Pb (1)	2 Bi	2 Po	—	0 Rn
—	6 Ra (1)(5)	3 Ac	3 Th (1)	3 Pa (1)	3 U												

* Also elements 58–71.

Elements inside of block are those that are caught in the General Procedure.

Elements outside of block are those that escape precipitation if they occur alone. Of these, boron, carbon, and fluorine are usually removed before the analysis is started, and phosphorus may necessitate special treatment before the NH_4OH Group is precipitated.

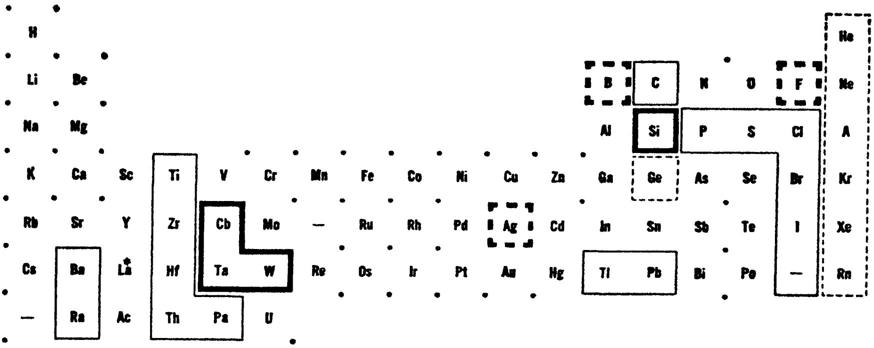
The number (or numbers) in parentheses below an element denotes the group (or groups) in which the element may appear as a result of factors such as incomplete precipitation in its own group, coprecipitation, or interaction with other elements. Germanium is marked 0 above and 2 below because ordinarily it is completely lost by volatilization during evaporation with hydrochloric acid, but it would fall in the H_2S group if it remained in the solution.

The number above an element denotes the group in which the element appears when it occurs alone.

TABLE 19

Acid Group

(Separation by evaporation with hydrochloric acid)


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that may be precipitated practically completely.

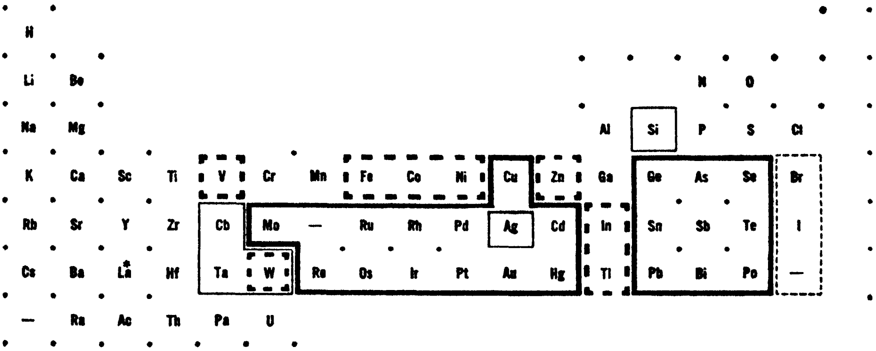
Heavy broken blocks inclose elements that interfere seriously and must be removed before the Acid Group is separated.

Light solid blocks inclose elements that may cause difficulties. Of these, carbon is usually removed at the start of the analysis.

Light broken blocks inclose elements that are definitely lost in preparing the solution for analysis, or during the evaporation.

TABLE 20

Hydrogen Sulphide Group


H
Li Be N O
Na Mg Al Si P S Cl
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po —
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose members of the Hydrogen Sulphide Group.

Heavy broken blocks inclose non-members of the group that may be precipitated in part under certain conditions.

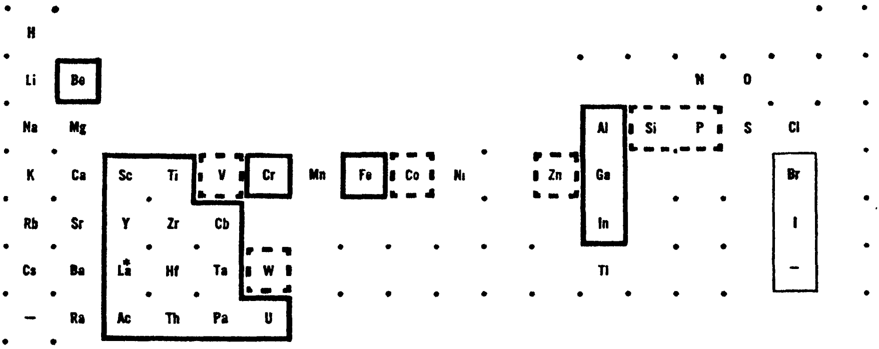
Light solid blocks inclose elements that may still be present in small amount through incomplete precipitation of the Acid Group.

Light broken blocks inclose elements that are left in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

TABLE 21

Ammonium Hydroxide Group



* Also elements 58–71.

Heavy solid blocks inclose members of the Ammonium Hydroxide Group.

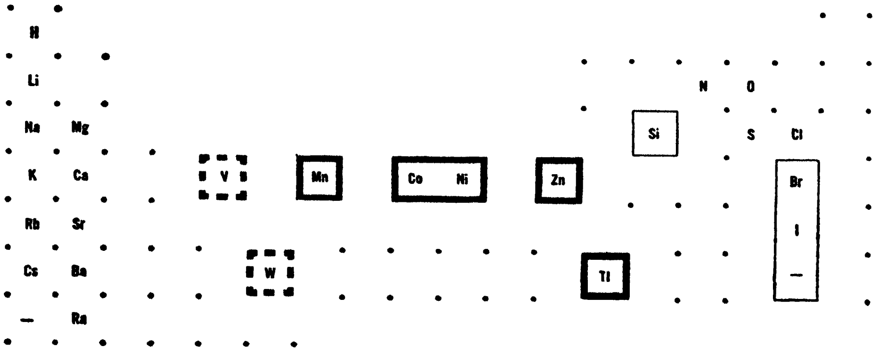
Heavy broken blocks inclose elements that may be caught in the precipitate (Si, P, V, and W more or less completely, and Co and Zn only partially).

Light solid blocks inclose elements that are still present in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

TABLE 22

Ammonium Sulphide Group



Heavy solid blocks inclose members of the Ammonium Sulphide Group.

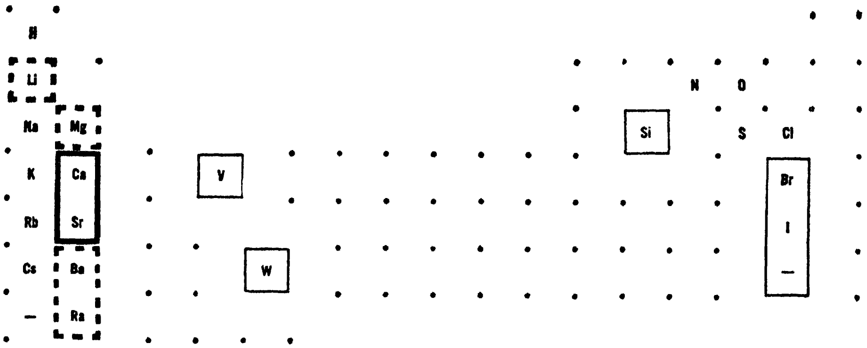
Heavy broken blocks inclose elements that may be carried down by members of the group.

Light blocks inclose elements that are left in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

TABLE 23

Ammonium Oxalate Group



Heavy solid blocks inclose members of the Ammonium Oxalate Group.

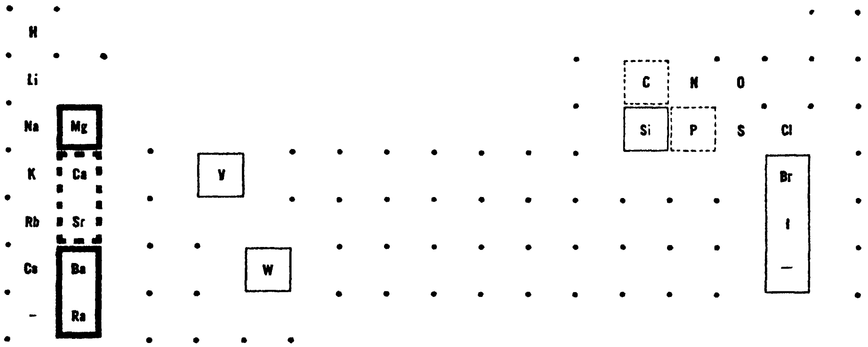
Heavy broken blocks inclose elements that may be present and may interfere by coprecipitation.

Light blocks inclose elements that are left in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

TABLE 24

Ammonium Phosphate Group



Heavy solid blocks inclose members of the Ammonium Phosphate Group.

Heavy broken blocks inclose elements which may not be completely precipitated by ammonium oxalate and which are then precipitated at this point.

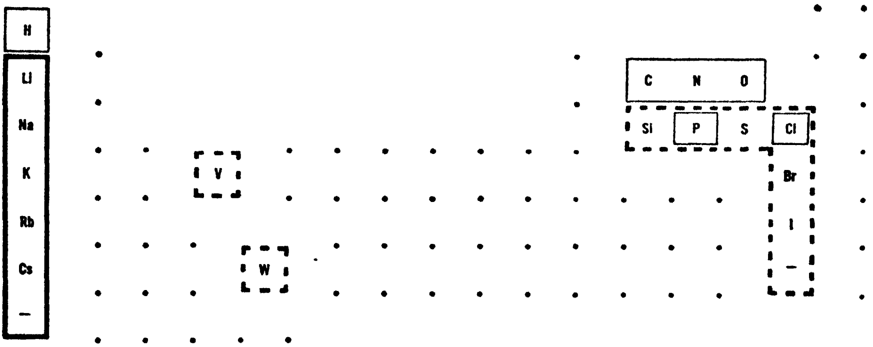
Light unbroken blocks inclose elements that are left in solution only under exceptional conditions.

Light broken blocks inclose elements that have been reintroduced.

Missing elements are those that have been removed in the General Procedure.

TABLE 25

Elements That May Be Left in Solution at the Conclusion of the General Procedure



Heavy blocks inclose elements originally present in the sample, which are left in solution.

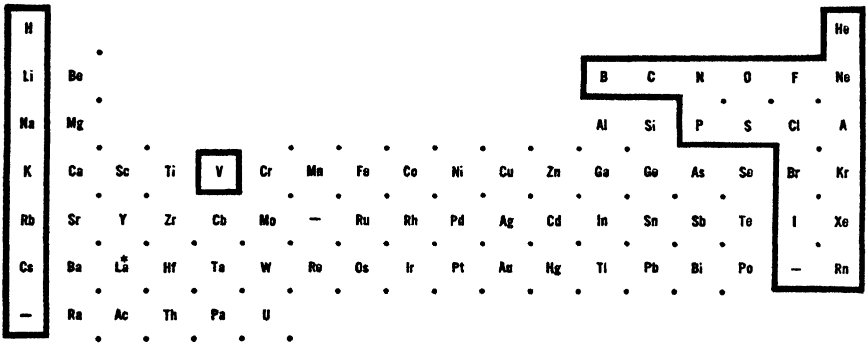
Heavy broken blocks inclose elements originally present in the sample, which may be present if certain conditions have prevailed.

Light blocks inclose elements introduced during the analysis.

Missing elements are those that are removed in the General Procedure.

TABLE 26

Elements That Are Not Caught in the General Procedure If They Occur Alone

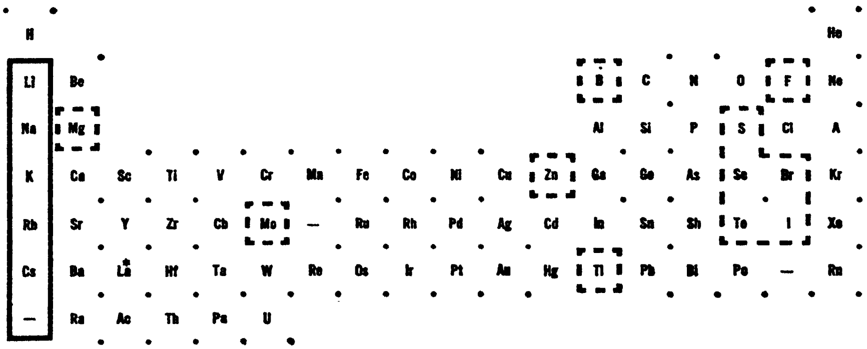

H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

The elements inclosed in heavy blocks do not form precipitates with any of the reagents used in the separations of the groups and are therefore not caught if they occur alone.

TABLE 27

Alkali Group



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

* Also elements 58–71.

Solid blocks inclose members of the Alkali Group.

Broken blocks inclose elements that may accompany the alkalies in the J. L. Smith method.

CHAPTER VII

SEPARATION OF THE ACID GROUP

A number of elements form acids instead of salts when they are subjected to attack by mineral acids such as hydrochloric, sulphuric, perchloric, or nitric. Some of the acids thus formed are quite insoluble, and so the treatment is often used for the separation of the elements (the Acid Group) that form insoluble acids from the elements that do not. The behavior of these acid-forming elements is not necessarily the same with each mineral acid, or in all combinations with other elements. Some, like silicon and tungsten, can be separated quite well by treatment with any of the four commonly used acids; some, like tin and antimony, can be separated by treatment with one acid but not with another; and some, like columbium and tantalum, can be separated when alone, but not when associated with certain other elements.

All these insoluble acids are white except those of vanadium and tungsten, which are reddish-brown and yellow, respectively. None of the acids is completely precipitated. Therefore further separations are in order if all the element is sought, or if the dissolved portion would interfere in subsequent treatments of the solution.

The insoluble acids will, of course, be contaminated by other compounds if ions that react to form insoluble compounds are present in the material that is analyzed, or are introduced during the analysis. Thus, the acids may be contaminated by insoluble phosphates such as zirconium phosphate, insoluble sulphates such as barium sulphate, insoluble halides such as silver chloride, or insoluble perchlorates such as potassium perchlorate.

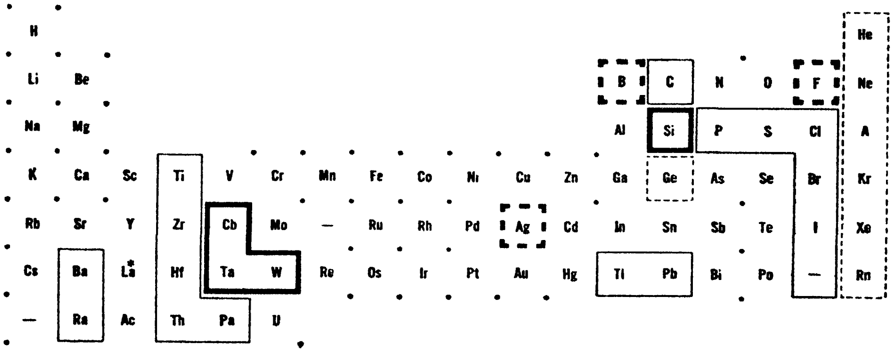
The treatments commonly used in separations of the insoluble acids, and the results to be expected, are described in the following sections. Of the four treatments, digestion with hydrochloric acid is the one most used in analyses made according to the General Procedure. In all the separations the discussion centers around silicon, which is reported as silica in analyses of oxidized materials such as rocks, and as silicon in analyses of metals. It is understood, of course, that the filtrates left after the separations of the insoluble acids are reserved for further investigations (see Hydrogen Sulphide Group, page 49).

A. Elements Precipitated by Digestion with Hydrochloric Acid

In this method, which is commonly used for determining the percentage of SiO_2 in materials such as rocks, minerals, and ceramic products, silicic acid is formed by direct treatment with hydrochloric acid or by fusion with a suitable flux followed by solution of the melt in hydrochloric acid. The silicic acid is next dehydrated and thus rendered insoluble by evaporating the solution to dryness, and is then recovered by drenching the residue with hydrochloric acid, diluting with water, filtering, and washing the residue. The recovery of the silicic acid is never quite complete in spite of repeated evaporations, and the acid is never pure. The silicic acid remaining in solution after two evaporations is usually ignored. The silicic acid that is obtained is ignited and weighed as impure silica, after which the true silica content is found by treating the silica with hydrofluoric and sulphuric acids, evaporating to volatilize the silicon as the tetrafluoride, igniting, and subtracting the weight of the impurities that are left.

TABLE 28

Separation of the Acid Group by Evaporation with Hydrochloric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that may be precipitated practically completely.

Heavy broken blocks inclose elements that interfere seriously and must be removed before the Acid Group is separated.

Light solid blocks inclose elements that may cause difficulties. Of these, carbon is usually removed at the start of the analysis.

Light broken blocks inclose elements that are definitely lost in preparing the solution for analysis or during the evaporation. (See also Table 14, page 29.)

The chief considerations in such a determination of silica are (1) that no significant amounts of silicic acid be lost, (2) that the weight of the contaminants must not change as a result of the treatment with sulphuric and hydrofluoric acids, and (3) that the amount of the contaminants must not be so large as to render the expulsion of hydrofluoric and sulphuric acids and the subsequent ignition difficult. The elements that may accompany silica or cause difficulties in such a procedure are shown in Table 28.

Fortunately, the chief troublemakers, boron and fluorine, are seldom encountered. Boron causes high results for silica because some of it is carried down by silicic acid, weighed with the impure silica, and then volatilized as boron trifluoride. Fluorine causes low results because it reacts with silicic acid to form volatile silicon tetrafluoride during the evaporation with hydrochloric acid. In accurate determinations of silicon, boron must be expelled by special treatments with methyl alcohol at the outset of the analysis, and fluorine must be separated by special treatments before the solution is acidified.

Columbium, tantalum, tungsten, and silver may separate almost completely with the silicic acid. The first two are seldom encountered and are objectionable chiefly because they render the treatment of the impure silica more difficult. The completeness of their separation is affected by elements such as titanium or zirconium. Tungsten, which is more common, requires special attention during the two ignitions, for tungstic oxide begins to volatilize at a temperature as low as 850°C. Silver is precipitated as a halide and not as an insoluble acid. If silver is present in the material, it must be removed before digesting with hydrochloric acid, or else the dehydration must be made in nitric or perchloric acid solution.

Gold and palladium separate as metal to a slight extent; osmium tends to form a crust on the evaporating dish. More or less gold is lost by volatilization if nitric-hydrochloric acid solutions are rapidly evaporated to dryness. Phosphorus, sulphur, chlorine, bromine, and iodine form insoluble compounds with certain elements and then cause difficulties. Phosphorus, for example, reacts with zirconium, titanium, hafnium, thorium, and protoactinium to form insoluble phosphates which survive the first ignition and then lose more or less phosphoric acid by volatilization during the subsequent treatment, thus causing high results. Sulphur, as sulphate, reacts with barium and lead to form insoluble sulphates, which render the final evaporation and ignition (especially with lead) difficult. The halogens react with silver, also lead and univalent thallium if present in large quantities, to form insoluble halides, which are changed to sulphates in the final treatment, and so cause low results.

During the evaporations with hydrochloric acid, arsenic (trivalent) and germanium are completely volatilized, and certain other elements may be partially volatilized as noted in Chapter IV C (page 28). Selenium, tellurium, and vanadium are reduced to the quadrivalent state; thallium (trivalent) is partially reduced to the univalent state; and oxidized chromium and manganese compounds are reduced to the tri- and di- states, respectively.

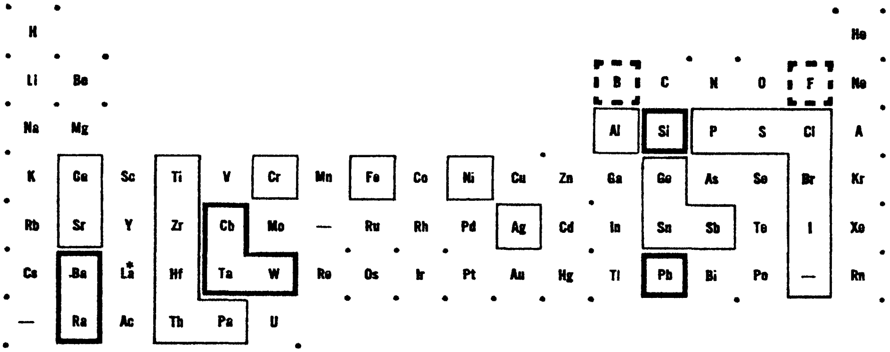
B. Elements Precipitated by Digestion with Sulphuric Acid

In this method, silicic acid is obtained in dilute sulphuric acid solution, dehydrated by heating until the acid fumes strongly, and recovered by diluting with water, filtering, and proceeding as in the hydrochloric acid method. Special care must be taken in the choice of the crucible and the method of ignition if elements such as lead, tin, or antimony are present. This precaution is necessary in the next two methods as well.

Digestion with sulphuric acid is more often used in analyses of metals than in analyses of rocks, minerals, ores, and ceramic products. In the latter, the silicon occurs as silicate, and the silicic acid is obtained in sulphuric acid solution by fusing with a suitable flux and dissolving the melt in the diluted acid. In most metals, the silicon is present, as silicide, in the combined state. It is then easily converted to silicic acid by attack with acids. Occasionally, part of the silicon is present in the free state, which resists attack by acids. In this case the free silicon is usually gathered with the silicic acid, which is ignited, fused with sodium carbonate to convert the free silicon to sodium silicate, and the melt dissolved and treated as with rocks.

TABLE 29

Separation of the Acid Group by Evaporation with Sulphuric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy blocks inclose elements that may be precipitated practically completely.
Heavy broken blocks inclose elements that interfere seriously.
Light blocks inclose elements that may cause difficulties.

The elements that may accompany silica, or cause difficulties in its determination by such procedures, are shown in Table 29.

As in evaporations with hydrochloric acid, boron and fluorine are the chief troublemakers. Columbium, tantalum, tungsten, lead, barium (and radium) may be precipitated almost completely, the first three as insoluble acids, and the others as insoluble sulphates. The effects of these compounds have been discussed in A. Sulphates of strontium and calcium may be precipitated in part if appreciable amounts of the elements are present. In a different category are the difficultly soluble anhydrous sulphates of aluminum, chromium, iron, and nickel that are formed if the evaporation with sulphuric acid is prolonged at high temperatures or carried to dryness. If left with the silicic acid, these yield oxides on ignition and render the subsequent treatment with hydrofluoric and sulphuric acids difficult, or even impossible if large quantities are present.

Tin and, to a less extent, germanium and antimony hydrolyze in dilute sulphuric acid solution and may therefore accompany silicic acid. These then require care during the ignition of the silica and add to the difficulties of the treatment with hydrofluoric and sulphuric acids. Phosphorus may interfere, as discussed in A, if elements such as zirconium, hafnium, titanium, thorium (and protoactinium) are present. Evaporations with sulphuric acid cause complete expulsion of halogens from soluble halides (but not from silver halides), and more or less loss of phosphorus if carried on for prolonged periods at temperatures much above the fuming point. Osmium and rhenium may be volatilized in part if sulphuric acid alone is used. Under these conditions the members of the platinum group other than osmium are not volatilized, but may be reduced to some extent and deposited as metal. Gold is deposited as metal to some extent, and more or less may be lost by volatilization. If nitric acid was present at the start, osmium may be completely, and ruthenium and rhenium incompletely, volatilized (see Chapter IV C, page 28).

C. Elements Precipitated by Digestion with Perchloric Acid

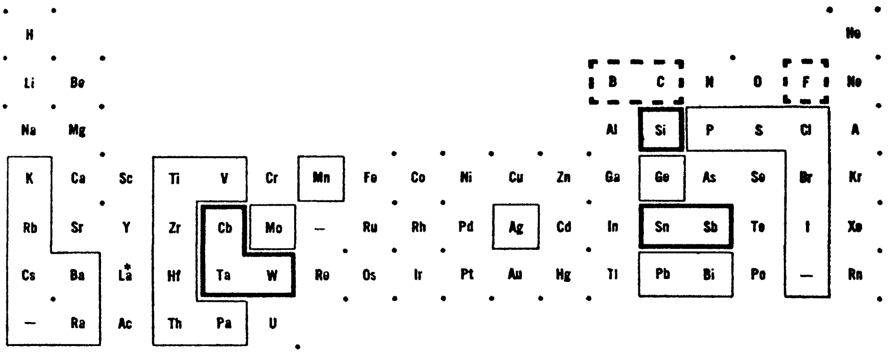
In this method, a solution containing perchloric and silicic acids is heated until fumes of perchloric acid are evolved, then *boiled* for 10 to 15 minutes, and finally cooled, diluted with water, and filtered as in the hydrochloric acid method. Silicic acid that is so obtained is likely to decrepitate during ignition, unless it has been washed moderately with warm diluted hydrochloric acid (1 + 1) before the final washing with water. The perchloric acid method is used in analyses of both metals and minerals. With minerals it is usually necessary to fuse with a suitable flux and to dissolve the melt in the diluted acid. Occasionally, as with chromite, a mixture of perchloric and sulphuric acids is more efficacious than perchloric acid alone. Metals are usually broken up by direct attack with the acid, attack with sulphuric and perchloric acids, or attack with hydrochloric and nitric acids followed by addition of perchloric acid. Further treatments, as described under Digestion with Sulphuric Acid, are needed if the metals contain free silicon, for the acid attack does not convert free silicon to silicic acid.

The elements that may accompany silicic acid, or cause difficulties in the perchloric acid method, are shown in Table 30.

As in the other methods, boron and fluorine are the chief troublemakers. Carbon does not cause trouble in the determinations of silicon or silica, but is mentioned so as to call attention to the danger of a serious explosion if perchloric acid is heated to the fuming point in the presence of easily oxidized organic compounds. Danger from this source can be avoided by adding nitric acid before the temperature is raised above 100°C. Tungsten, columbium, tantalum, tin, and antimony may be almost completely precipitated as acids, although in certain combinations, as for example small amounts of columbium associated with large amounts of titanium, little or no precipitation may take place. Molybdenum, germanium, vanadium, manganese, and bismuth may be precipitated in part if they are present in large amounts. Insoluble sulphates, halides, and phosphates are decomposed but slowly when fumed with perchloric acid, and so accompany the silicic acid if appreciable amounts of the reacting elements are present. Potassium, rubidium, cesium (and also the ammonium ion) are precipitated as the sparingly soluble perchlorates if large amounts of these elements are present. Repeated evaporations with perchloric acid cause partial volatilization of rhenium, and complete volatilization of osmium, ruthenium, and of halogens from soluble halides. Gold is not volatilized, even when solutions containing nitric, hydrochloric, and perchloric acids are heated to copious fumes of the latter (about 205°C). An interesting effect is the almost complete oxidation of chromium from the tri- to the sexivalent state, and the volatilization of chromium if hydrochloric acid is added to the fuming solution.[1]

TABLE 30

Separation of the Acid Group by Evaporation with Perchloric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy blocks inclose elements that may be precipitated practically completely.
Broken blocks inclose elements that interfere seriously.
Light blocks inclose elements that may cause difficulties.

D. Elements Precipitated by Digestion with Nitric Acid

In this method, a solution containing nitric and silicic acids is evaporated to dryness, drenched with warm concentrated nitric acid, warmed, diluted with hot water, and the impure silicic acid recovered by filtering and washing the residue with hot water. The method is not often used for the determination of silicon, chiefly on account of the sparing solubility of certain nitrates. In a modified form (see page 210) it is often employed to separate tin and antimony in analyses of bronze and similar alloys.

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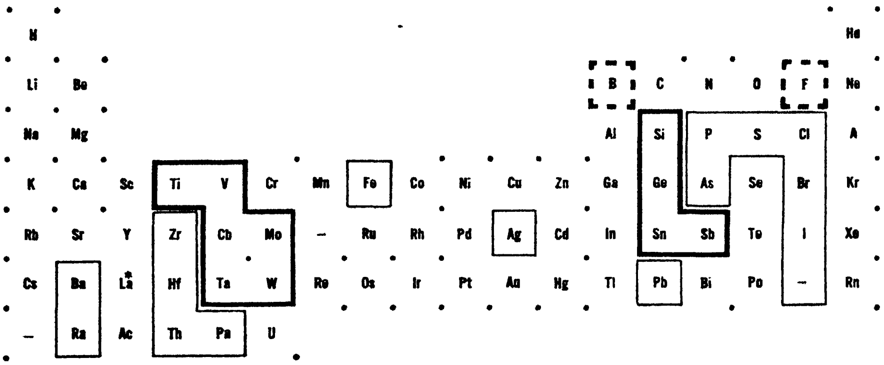
[1] Private communication from C. B. Francis, Carnegie-Illinois Steel Corporation, concerning a method originating with Fred W. Smith of their South Works Laboratory, L. P. Chase, Chief Chemist, South Chicago, Ill.

The elements that may accompany silicic acid, or cause difficulties in the nitric acid method, are shown in Table 31. Of these, boron and fluorine interfere as they do in the other methods. It will be noted that the number of elements that form insoluble acids which accompany the silicic acid is larger than in the other methods. Arsenic and phosphorus may be carried down quantitatively by elements such as tin or antimony. Gold, iridium, and palladium may be deposited to some extent as a scum on the residue or as a crust on the dish. Arsenic, molybdenum, or phosphorus tends to prevent complete precipitation of tungsten, and iron renders separation of tin incomplete. Insoluble chlorides, sulphates, and phosphates are not decomposed by evaporation with nitric acid, and will be found in the residue if appreciable amounts of the reacting elements are present. Halogens are completely (fluorine with difficulty) expelled from soluble halides. Osmium may be volatilized completely, and ruthenium incompletely. More or less gold is volatilized if solutions containing aqua regia are rapidly evaporated to dryness.

TABLE 31

Separation of the Acid Group by Evaporation with Nitric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo – Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po – Rn
– Ra Ac Th Pa U

* Also elements 58–71.
Heavy blocks inclose elements that may be precipitated practically completely.
Broken blocks inclose elements that interfere seriously.
Light blocks inclose elements that may cause difficulties.

CHAPTER VIII

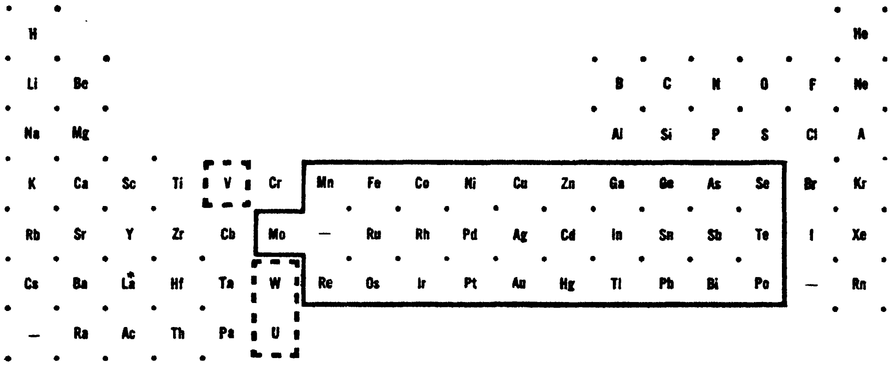
SEPARATION OF THE HYDROGEN SULPHIDE GROUP

A. Elements That Form Insoluble Sulphides

Thirty-three of the elements (see Table 32) form insoluble sulphides that are of use in analytical chemistry. Twenty-two of these, the Hydrogen Sulphide Group, form insoluble sulphides if fairly strong (approximately 0.3 *N*) acid solutions containing their ions are treated with hydrogen sulphide.[1] Such solutions are too acid for the precipitation of the sulphides of zinc, indium, thallium, gallium, nickel, cobalt, iron, manganese, vanadium, tungsten, and uranium.[2] Of these, zinc and indium can be pre-

TABLE 32

Elements That Form Insoluble Sulphides


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that form insoluble sulphides useful in both qualitative and quantitative analysis.

Heavy broken blocks inclose elements that form insoluble sulphides useful only in qualitative analysis.

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[1] The precipitates obtained with selenium and tellurium are not true sulphides, but mixtures of the elements, sulphur, and probably sulphides.

[2] The sulphides of vanadium, tungsten, and uranium are utilized in certain schemes of qualitative analysis, seldom if ever in quantitative analyses. None are precipitated by hydrogen sulphide when they occur alone in moderate concentrations of mineral acid. In buffered acid solutions precipitation is incomplete with vanadium, very incomplete with uranium, and slight if any with tungsten. Uranyl sulphide, UO_2S, is brown and quite insoluble in solutions containing ammonium sulphide. Vanadium sulphide, V_2S_5, is dark brown and quite, though not readily, soluble in ammonium sulphide, to which it imparts a reddish-brown, green, or purple color depending on conditions. Addition of acid to such solutions causes incomplete precipitation of V_2S_5. Tungsten sulphide, WS_3, is brown to black in color and readily soluble in ammonium sulphide, to which it imparts a brown color. From such solutions, acids precipitate WS_3 incompletely.

cipitated in solutions containing mineral acids, but the final acid concentration must be very low, not above 0.01 *N* with zinc, or 0.025 *N* with indium (both preferably in sulphuric acid solution). The others cannot be completely precipitated, even in neutral solutions of their inorganic salts, except thallium (univalent) and gallium which are precipitated from neutral or slightly acid solutions provided certain other sulphide-forming elements, such as copper or arsenic, are present. Thallium (univalent) can also be precipitated in buffered solutions[3] of certain organic acids, such as solutions containing acetic acid and sodium acetate, or tartaric acid and ammonium tartrate; the same is true of gallium if certain sulphide-forming elements are present. Nickel and cobalt can also be precipitated, though not quite quantitatively, in buffered solutions. Under these conditions iron sulphide is incompletely precipitated, and manganese not at all. For the precipitation of manganese, and the complete precipitation of iron, an alkaline solution is needed. Such solutions cause no precipitation of gallium unless it is associated with certain other precipitable elements. Solutions of alkaline sulphides, in turn, dissolve some of the sulphides that are insoluble in acids. These differences in behavior enable the analyst to separate sulphide-forming elements from other elements, and certain sulphide-forming elements from each other.

Solutions of ammonium sulphide cause the precipitation of a number of elements (the Ammonium Hydroxide Group) that do not form sulphides. To simplify quantitative analyses it is therefore customary to separate the members of the Hydrogen Sulphide Group, and then to remove the members of the Ammonium Hydroxide Group before proceeding with the precipitation of the other sulphide-forming elements (the Ammonium Sulphide Group). The separations will therefore be described in this order, rather than in the direct sequence that would be followed if only sulphide-forming elements were involved.

B. Elements That Are Precipitated by Hydrogen Sulphide in Strong (pH < 1) Acid Solution

There is no simple procedure that yields complete precipitation of all the elements that form sulphides in acid solution. The difficulties that attend precipitation in hydrochloric or sulphuric acid solutions are illustrated in

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[3] Buffered solutions are solutions that resist any marked change in hydrogen-ion concentration. Solutions that oppose any marked increase in acidity contain a weak acid together with enough of a soluble salt of that acid to repress the ionization of the acid and to take care of any stronger acid that may be introduced. Thus, if thallous sulphide (Tl_2S) is precipitated by passing hydrogen sulphide into a solution containing thallous sulphate (Tl_2SO_4), acetic acid, and sodium acetate, the sulphuric acid which is liberated reacts with the acetate to yield neutral sodium sulphate and acetic acid. The ionization of the latter is small and is repressed by the acetate which still remains, and so the acidity remains essentially as it was at the start.

Table 33. In these precipitations all but those in 18 *N* and 36 *N* sulphuric acid were made by heating 100 ml of a solution containing about 20 mg of the element in question to 90–100°C, passing a rapid current of hydrogen sulphide through the solution for 15 minutes as it cooled, and then allowing the solution to stand for 1 hour. With the 18 *N* and 36 *N* solutions the gas was passed into the cool solution for 30 minutes, after which they were filtered immediately.

Nearly all the silver is precipitated as chloride in the concentrations of hydrochloric acid shown in the table, but that which remains in solution is not completely precipitated by hydrogen sulphide in 3 *N* or stronger acid. Similarly, the small amounts of lead that remain unprecipitated as sulphate in the concentrations of sulphuric acid shown in the table are not precipitated by hydrogen sulphide in solutions stronger than 0.5 *N*. In the last, complete precipitation can be obtained by adding a drop of ammonium hydroxide while the hydrogen sulphide is passed into the solution. This "seeding out" is almost always necessary in precipitating small quantities of lead with hydrogen sulphide.

It will be noted that, except with cadmium, indium, lead, and possibly molybdenum, precipitations in *N* hydrochloric acid solutions are as satisfactory as in 0.2 *N* solutions. A few elements such as arsenic and quadrivalent selenium or tellurium can be quantitatively precipitated in much stronger (approximately 12 *N*) hydrochloric acid solution. Sulphuric acid solutions can be used in full strength (36 *N*) with a surprisingly large number of the elements, and concentrations as high as 6 *N* are permissible except with cadmium, lead, molybdenum, and possibly a few others. As a matter of fact, the stronger acids are preferable in precipitations of elements such as germanium, rhenium, or quinquevalent arsenic in hydrochloric acid solution, or germanium, platinum, rhenium, or quinquevalent arsenic in sulphuric acid solution.

Molybdenum, rhenium, and the platinum metals, excepting palladium, require special treatments for complete precipitation. Molybdenum, for example, requires a longer period of digestion with hydrogen sulphide, and it is usually necessary to oxidize the filtrate first obtained and repeat the treatment with hydrogen sulphide in order to obtain the last of the molybdenum. With heptavalent rhenium, precipitation can be rendered complete by prolonged treatment at the higher (4 *N* HCl or 6 *N* H_2SO_4) acidities. Platinum, likewise, is more easily precipitated in higher concentrations of sulphuric acid than in 0.5 *N* acid, but precipitation can be complete at the lower acidities, provided that the hot solution is gassed for ½ to 1 hour and a longer period of digestion is allowed. Rhodium and iridium are more readily precipitated in hydrochloric than in sulphuric acid solutions, but complete precipitation of these, as well as of osmium and ruthenium, is difficult. With iridium, for example, gassing with hydrogen

TABLE 33

Precipitation of Sulphides in Acid Solutions

Element and Valence	Normality of HCl					Normality of H_2SO_4					Color of Sulphides
	0.2 *N*	0.5 *N*	*N*	3 *N*	6 *N*	0.5 *N*	3 *N*	6 *N*	18 *N*	36 *N*	
Ag^{I}	C	C	C	I	I	C	C	C	C	C	Black
As^{III}	C	C	C	C	C	C	C	C	C	C	Yellow
As^{V}	I	I	I	I	C	I	I	I	C	C	Yellow
Au^{III}	C	C	C	C	C –	C	C	C	C	C	Brownish-black
Bi^{III}	C	C	C	N	N	C	C	C	C	I	Black
Cd^{II}	C	C –	I	N	N	C	I	N	N	N	Yellow
Cu^{II}	C	C	C	C	I	C	C	C	C	C	Black
Ge^{IV}	I –	I	I	I	C	I –	I	C	C –	I	White
Hg^{II}	C	C	C	C	C	C	C	C	C	C	Black
In^{III}	I	N	N	N	N	N	N	N	N	N	Orange-yellow
Ir^{IV}	I	I	I	I	I	I	I	I	I –	N	Black
Mo^{VI}	C –	I	I	I	I –	C –	I	I –	I –	I –	Dark brown
Os^{IV}	I	I	I	I	N	I –	I –	I	I	I	Black
Pb^{II}	C	I	I	I –	N	I	N	N	N	N	Black
Pd^{IV}	C	C	C	C –	I	C	C	C	C	C	Brownish-black
Pt^{IV}	I	I	I	I	I	I –	I	C –	C	C –	“ “
Re^{VII}	I	I	I	I	I	I –	I	I	C –	I	“ “
Rh^{III}	I	I	I	I	I	I	I	I	I	I	“ “
Ru^{IV}	I	I	I	I	I	C –	I	I	I	I	“ “
Sb^{III}	C	C	C	C –	N	C	C	C	C	C	Orange-red
Sb^{V}	C	C	C	C –	I	C	C	C	C	C	“ “
Se^{IV}	C	C	C	C	C	C	C	C	C	C	Orange-yellow
Se^{VI}	I –	I	I	I	I	N	N	N	N	N	“ “
Sn^{II}	C	C	C	N	N	C	C	C	N	N	Brownish-black
Sn^{IV}	C	C	C	I	N	C	C	C	C	I	Yellow
Te^{IV}	C	C	C	C	C	C	C	C	C	C	Black
Te^{VI}	N	N	N	N	I	I –	I –	I –	I –	I –	Black

C = Complete; C – = Nearly complete; I = Incomplete; I – = Very incomplete; N = No precipitation.

sulphide for 2–3 hours in a hot 20 per cent hydrochloric acid solution is required for complete precipitation.

Most of the sulphides of the Hydrogen Sulphide Group are black or dark colored. Exceptions are those of germanium, which is white; arsenic, cadmium, and quadrivalent tin, which are yellow; and antimony and selenium, which are orange colored. The colors of the sulphides listed in Table 33 are those ordinarily obtained. Under certain conditions the colors of some of these may vary; for example, mercuric sulphide may be yellow when precipitated from 6 *N* hydrochloric acid solution.

In general practice, precipitations of the Hydrogen Sulphide Group are made in solutions approximately 0.3 *N* with respect to hydrochloric or sulphuric acid.

C. Elements That Are Precipitated by Hydrogen Sulphide in 0.2 – 0.5 *N* Acid Solution (The Hydrogen Sulphide Group)

After the members of the Acid Group have been removed in the General Procedure (p. 42), the next step is the removal of the members of the Hydrogen Sulphide Group in the reserved filtrate (page 42). As a rule, precipitations are started by passing hydrogen sulphide through hot solutions containing about twice the proper concentration of acid, and then completed by continuing the current of gas after the solution has cooled and has been diluted with an equal volume of water. Hydrochloric or sulphuric acid in final concentrations of 2.5 ml of the former or 1.5 of the latter per 100 ml (0.2–0.5 *N* acid solutions) are most often used, although cold dilute nitric acid or perchloric acid can be substituted if occasion demands. When precipitation is complete, the solution is filtered, and the precipitate is washed with diluted acid saturated with hydrogen sulphide and of the same strength as was used in the precipitation. The precipitate is then examined for the members of the Hydrogen Sulphide Group, the filtrate being reserved for the separation of the Ammonium Hydroxide Group (page 55).

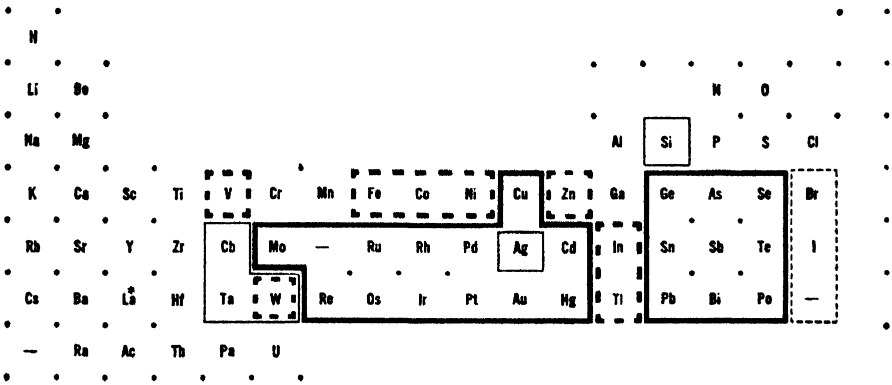
The elements that can be expected in a precipitate obtained under such conditions are shown in Table 34. Vanadium, tungsten, iron, cobalt, nickel, zinc, thallium, and indium (in moderate concentration) are not precipitated when alone. They may, however, be carried down to some extent by other members of the group. This is especially true of indium, and of thallium if it has not been reduced to the univalent state before treating with hydrogen sulphide. Contamination by iron, cobalt, nickel, zinc, indium, and thallium (univalent) is usually relatively slight and can be rendered negligible by modifying the precipitation procedure, as by repeating the precipitation or by using more acid. Coprecipitation of vanadium or tungsten can be avoided by adding tartaric acid before treating with hydrogen sulphide. Any thallium that remains in solution will be in the univalent state, for trivalent thallium is reduced by hydrogen sulphide in acid solution.

Rocks contain very little, if any, of the members of the Hydrogen Sulphide Group (see Table 15, page 33); thus in rock analysis the treatment with hydrogen sulphide in acid solution serves chiefly for the removal of platinum metals that may have been introduced through fusions or evaporations in platinum vessels. In general analytical work, on the other hand, the treatment is a very important operation, for it serves for the more or less complete separation of at least twenty-two of the elements from the others.

TABLE 34

Members of the Hydrogen Sulphide Group

Elements that are precipitated by hydrogen sulphide in 0.2 — 0.5 N solutions of hydrochloric or sulphuric acid


H
Li Be N O
Na Mg Al Si P S Cl
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po —
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose members of the Hydrogen Sulphide Group.

Heavy broken blocks inclose non-members of the group that may be precipitated in part under certain conditions.

Light solid blocks inclose elements that may still be present in small amount through incomplete precipitation of the Acid Group.

Light broken blocks inclose elements that are left in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

CHAPTER IX

SEPARATION OF THE AMMONIUM HYDROXIDE GROUP

A. Elements That Are Precipitated by Ammonium Hydroxide in a Solution from Which the Members of the Acid Group and Hydrogen Sulphide Group Have Been Removed

After the members of the Acid and Hydrogen Sulphide Groups have been removed in the General Procedure (pages 42 and 49), the next step is the precipitation of the members of the Ammonium Hydroxide Group. This is done by boiling the acid filtrate that was left after the separation of the Hydrogen Sulphide Group until hydrogen sulphide is expelled, oxidizing to make sure that iron is trivalent, adding diluted ammonium hydroxide until the *p*H of the solution lies between 6.5 and 7.5, and boiling for 1–3 minutes. The solution is filtered as soon as the precipitate settles, and the precipitate is washed. With some substances (certain rare earths), the *p*H must be higher than 7.5; with others (iron for example), the hydrogen-ion concentration of the solution need not be adjusted so carefully, and some precipitates must be washed with special solutions. The filtrate and washings are saved for the precipitation of the Ammonium Sulphide Group.

Colors of the precipitates obtained in the Ammonium Hydroxide Group are quite the reverse of those obtained in the Hydrogen Sulphide Group, for most are white, and only a few are dark colored. Exceptions are those of trivalent iron (brown), sexivalent uranium (yellow), trivalent chromium (gray-green), and certain rare earths, such as samarium (yellowish-white), erbium (pink), praseodymium (green), and neodymium (blue). Trivalent cerium is white, but gradually changes to yellow to brown through oxidation.

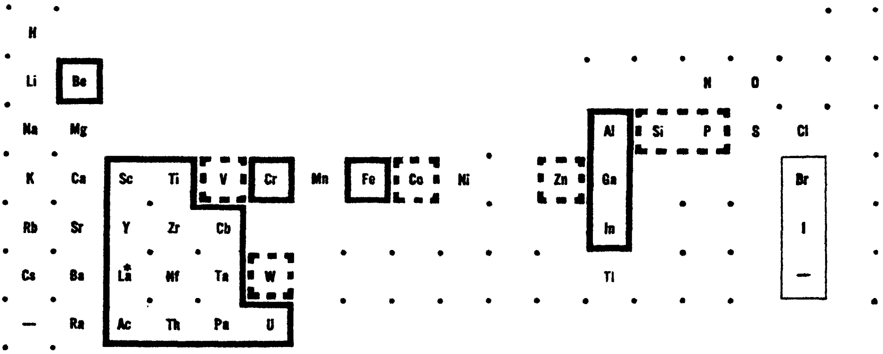
The precipitate is ignited in accordance with the properties of the oxide or oxides that are expected; thus, aluminum oxide can be ignited at 1200°C and is not harmed in a reducing atmosphere, whereas iron oxide should not be heated at temperatures above 1100°C and must be kept in an oxidizing atmosphere.

The elements that may be expected in precipitates obtained under the conditions that have been described are shown in Table 35. Of these, it will be noted that 32 (counting all the rare earths, and assuming that the thallium remains in the univalent state during the oxidation of the iron) can be quantitatively precipitated. None of the others is precipitated if it occurs alone. The amount of cobalt or zinc that may be carried down by members of the group may be appreciable, but is usually only a small part of the total amount present. On the other hand, all the silicon, phosphorus, vanadium, and tungsten may be found in the precipitate if they are present in the proper ratio to the precipitable elements. If phosphorus exceeds this ratio, it causes precipitation of members, such as manganese, calcium, and magnesium, of the succeeding groups. Such cases are relatively rare and require special treatments before the precipitation of the Ammonium Hydroxide Group is attempted. For these reasons phosphorus will rarely be found in the filtrate in a well-ordered analysis.

TABLE 35

Members of the Ammonium Hydroxide Group

Elements that are precipitated by ammonium hydroxide in a solution from which boron, carbon, fluorine, and the members of the Acid (Table 28, page 43) and Hydrogen Sulphide (Table 34, page 54) Groups have been removed.



* Also elements 58–71.

Heavy solid blocks inclose members of the Ammonium Hydroxide Group.

Heavy broken blocks inclose elements that may be caught in the precipitate (Si, P, V, and W more or less completely and Co and Zn only partially).

Light solid blocks inclose elements that are still present in solution only under exceptional conditions.

Missing elements are those that have been removed in the General Procedure.

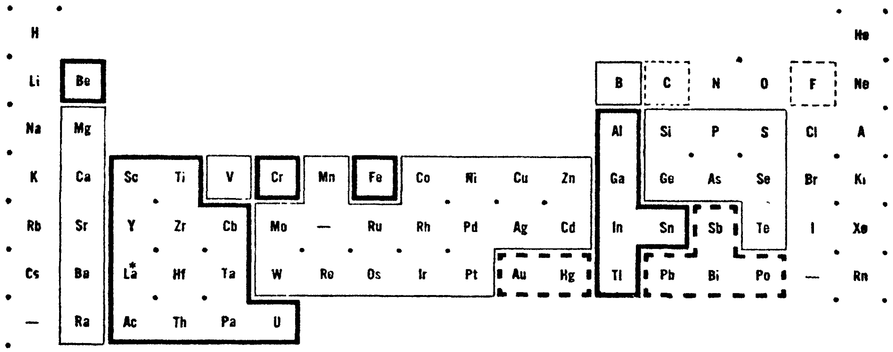
In rocks, elements of atomic numbers above that of iron (26) are present in very small amount if at all; consequently the precipitate produced by ammonium hydroxide is chiefly composed of aluminum and iron, together with more or less silicon, titanium, vanadium, phosphorus, and, if they are present in the rock, zirconium and chromium.

B. Elements That Are Precipitated by Ammonium Hydroxide in a Solution from Which No Elements Have Been Removed

The number of elements that can be expected in an ammonium hydroxide precipitate is materially increased if the precipitation is made in solutions from which no elements have previously been removed. Thus, as is shown in Table 36, the number of elements that can be quantitatively precipitated is increased to 34, and the number of other elements that have one effect or another on the precipitation is increased to all but the alkalies, halogens, nitrogen, oxygen, and the noble gases. Of the elements that can be quantitatively precipitated, it should be remarked that thallium is completely precipitated as the reddish-brown hydroxide if it is in the trivalent state, and not at all if it is in the univalent state. Of the elements that affect the precipitation in one way or another: (1) some, like mercury, ruthenium, gold, lead, bismuth, and antimony (trivalent only), are precipitated in part; (2) some, like boron, cobalt, copper, zinc, cadmium, rhodium, and, to a lesser extent, osmium and iridium, are carried down by the precipitate; (3) some, like carbon (as carbonate), fluorine, silicon, phosphorus, sulphur, vanadium, arsenic, germanium, platinum, palladium, rhenium, tungsten, lithium, magnesium, and the alkaline earths, form precipitates through interaction with other compounds; and (4) some, like carbon (as carbonaceous matter) and fluorine, prevent complete precipitation. The elements listed under (2) are not precipitated when alone (save possibly rhodium) and are usually only partially carried down by precipitates produced by ammonium hydroxide. On the other hand, most of the elements listed under (1) and (3) may be completely precipitated under certain conditions. If, for example, a tenfold excess of iron in the trivalent state is present, precipitation of germanium, tellurium (both quadrivalent and sexivalent),

TABLE 36

Elements That May Be Found in Precipitates Obtained by Adding Ammonium Hydroxide to Solutions from Which No Elements Have Been Removed



* Also elements 58–71.
Heavy solid blocks inclose elements that can be quantitatively precipitated when alone.
Heavy broken blocks inclose elements that are incompletely precipitated when alone.
Light solid blocks inclose elements that may be caught in the precipitate.
Light broken blocks inclose elements that may prevent precipitation.

antimony (trivalent), and quinquevalent vanadium, phosphorus, and arsenic is complete, and that of tungsten, vanadium (quadrivalent), antimony (quinquevalent), and selenium (quadrivalent or sexivalent) is nearly so. The behavior of molybdenum under such conditions depends on how the precipitation is made, much of it being carried down if a slight excess of ammonium hydroxide is added to the solution, whereas so little is carried down when the solution is poured into an excess of ammonium hydroxide that complete separation can be obtained by reprecipitation.[1]

Sometimes the precipitate is ignited and weighed, and the result reported as "Percentage of R_2O_3 Group Elements." It is apparent that such a report is of use only if the constituent elements are known and are few in number, as in the analysis of a limestone or a cement.

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[1] See Hillebrand and Lundell, Applied Inorganic Analysis, page 251, John Wiley and Sons, New York, 1929.

CHAPTER X

SEPARATION OF THE AMMONIUM SULPHIDE GROUP

A. General Considerations

As has already been stated (page 49), the solutions that are used in the separation of the Hydrogen Sulphide Group (page 53) are too acid for the precipitation of the sulphides of zinc, indium, thallium, gallium, nickel, cobalt, iron, manganese, vanadium, tungsten, and uranium.

Four of these sulphide-forming elements—iron, indium, gallium, and uranium—are quantitatively caught in the Ammonium Hydroxide Group (page 55) in the General Procedure, and provision is made for them in the examination of the precipitate obtained with ammonium hydroxide. The others, with the exception of vanadium and tungsten, are precipitated by adding ammonium sulphide to the ammoniacal filtrate, and comprise the " Ammonium Sulphide Group " in the General Procedure.

The sulphides of cobalt, nickel, and thallium are black; the sulphide of manganese is white to flesh-colored; and the sulphide of zinc is white.

B. Elements That Are Precipitated by Ammonium Sulphide in Solutions from Which the Members of the Acid, Hydrogen Sulphide, and Ammonium Hydroxide Groups Have Been Removed

Separations of the Acid, Hydrogen Sulphide, and Ammonium Hydroxide Groups should leave all the manganese and nickel in solution if ordinary conditions prevail and the separations have been properly performed. Most of the cobalt and zinc should also be present, although a little is always carried down by the ammonium hydroxide precipitate and some is occasionally lost in the hydrogen sulphide precipitate. The amounts of thallium, vanadium, and tungsten that remain in solution depend on the nature and the quantity of the elements that have been removed. All the thallium will probably be present if no precipitate was obtained with hydrogen sulphide; on the other hand, little of it may remain if relatively large amounts of arsenic or antimony were precipitated. Very little or no tungsten will remain if careful separations of silicon have been made, and the ammonium hydroxide group was bulky. The amount of vanadium that is left will also be small if the ammonia precipitate was large in comparison with the amount of vanadium. On the other hand, most of the vanadium may be present if vanadium preponderated.

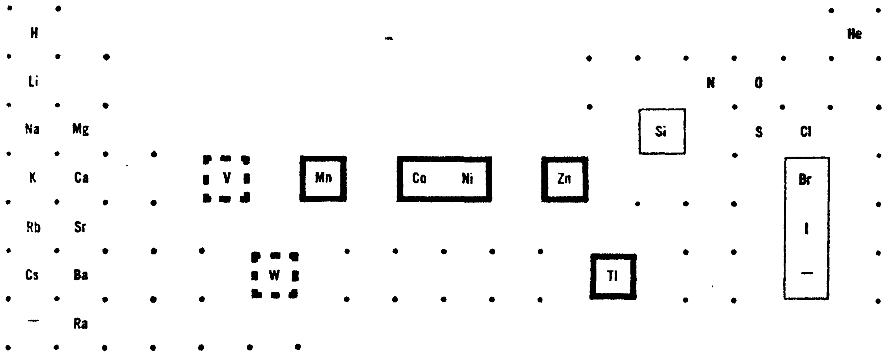
In the General Procedure, the Ammonium Sulphide Group is precipitated in an Erlenmeyer flask by (1) adding a fresh colorless solution of ammonium sulphide to the filtrate and washings left after the separation of the Ammonium Hydroxide Group (page 55); (2) filling the flask to the neck with water; (3) stoppering to exclude air; and (4) allowing the solution to stand for some time, usually overnight. The solution is then filtered and the sulphides washed with water containing a little ammonium chloride and colorless ammonium sulphide. The filtrate and washings are reserved for the precipitation of the Ammonium Oxalate Group (page 64).

The elements that are precipitated by such treatments are shown in Table 37. Of these, the precipitation of cobalt, zinc, and thallium can be made complete. Small amounts (of the order of 0.1–0.2 mg) of nickel and manganese may remain in solution. Vanadium and tungsten are not precipitated if they occur alone, but are carried down to a slight extent by the other sulphides. It is, of course, especially important that the ammonium sulphide be freshly prepared (free from sulphates) if barium, strontium, or appreciable amounts of calcium are present.

TABLE 37

Members of the Ammonium Sulphide Group

Elements that are precipitated by ammonium sulphide in a solution from which boron, carbon, fluorine, and the members of the Acid (Table 28, page 43), Hydrogen Sulphide (Table 34, page 54) and Ammonium Hydroxide (Table 35, page 56) Groups have been removed



Heavy solid blocks inclose members of the Ammonium Sulphide Group.
Heavy broken blocks inclose elements that may be carried down by members of the group.
Light blocks inclose elements that are left in solution only under exceptional conditions.
Missing elements are those that have been removed in the General Procedure.

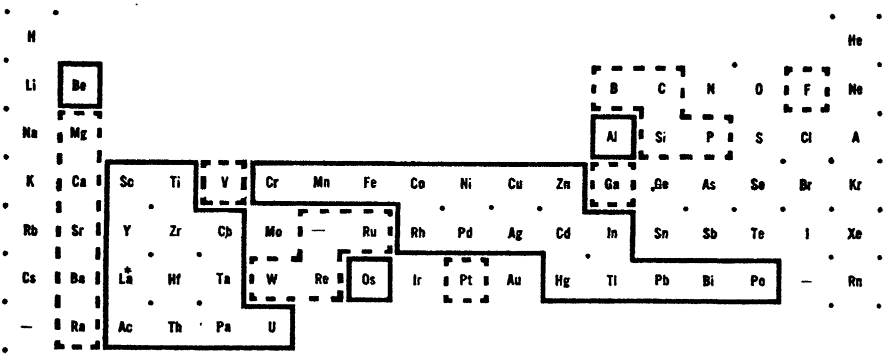
If the members of the Ammonium Sulphide Group are not removed, all save thallium (univalent) will be found in the succeeding groups. The amount of each that is caught with the Ammonium Oxalate Group is but a small part of that present, contamination by manganese being greatest and that by cobalt, nickel, and zinc diminishing in the order given. The amounts caught with the Ammonium Phosphate Group are somewhat larger, and range from complete precipitation of manganese to but very little of cobalt, nickel, and zinc, in the order given.

C. Elements That Are Precipitated by Ammonium Sulphide in Solutions from Which No Elements Have Been Removed

The elements that can be precipitated by ammonium sulphide if no prior separations have been made are shown in Table 38.

TABLE 38

Elements That May Be Found in Precipitates Obtained by Adding Ammonium Sulphide to Solutions from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose elements that are precipitated quantitatively or nearly so.
Broken blocks inclose elements that may interfere or be precipitated to some extent.

It will be noted that, in addition to the sulphides of the members of the Ammonium Sulphide Group, the precipitate will contain the sulphides of the members of the Copper Group and the hydroxides of the members of the Ammonium Hydroxide Group, except iron, uranium, and indium. It should be remembered that iron will yield the black sulphide instead of the reddish brown hydroxide, and so, because of its very common occurrence, usually hides the presence of other elements. Indium yields a sulphide that is white,[1] and uranium one that is brown. Of the elements that interfere or that are more or less precipitated, boron and silicon are carried down by members of the Ammonium Hydroxide Group. Vanadium and tungsten are carried down by members of the Hydrogen Sulphide (Copper Group), Ammonium Hydroxide, and Ammonium Sulphide Groups. Ruthenium and platinum are incompletely precipitated as sulphides. Carbon interferes by preventing complete precipitation of the Ammonium Hydroxide Group if the carbon is present in certain types of organic matter, and by causing precipitation of the alkaline earths if it is present as carbon dioxide. Phosphorus interferes because it reacts to form insoluble phosphates with members of the Ammonium Hydroxide Group, or with magnesium and the alkaline earths if it is present in excess of the amount which can enter into combination with the members of the Ammonium Hydroxide Group. Fluorine interferes because it prevents complete precipitation of certain members of the Ammonium Hydroxide Group, and forms insoluble fluorides with certain alkaline earths.

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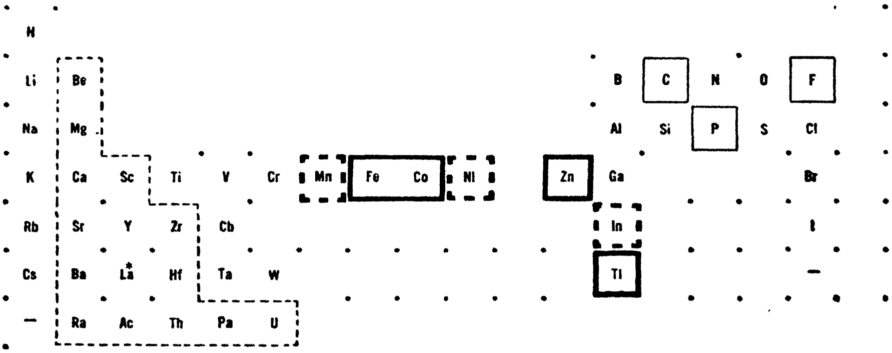
[1] Indium sulphide obtained from feebly acid solution is yellow to orange-yellow in color; the compound that is obtained with ammonium sulphide is white.

D. Elements That Are Precipitated by Ammonium Sulphide in Solutions Containing Ammonium Tartrate

In analyses in which the members of the Acid, Hydrogen Sulphide, and Ammonium Hydroxide Groups have been removed, there is no need to add ammonium tartrate before precipitating with ammonium sulphide, unless vanadium or tungsten happens to be present. Its use in such case prevents contamination of the precipitate by these elements, but at the same time has the drawback of preventing complete precipitation of manganese.

TABLE 39

Elements That May Be Found in Precipitates Obtained by Adding Ammonium Tartrate and Ammonium Sulphide to Solutions from Which Members of the Acid (page 42) and Hydrogen Sulphide (page 53) Groups Have Been Removed



* Also elements 58–71.

Heavy solid blocks inclose elements that are precipitated completely.

Heavy broken blocks inclose elements that are precipitated incompletely.

Light solid blocks inclose elements that may cause difficulties.

Light broken blocks inclose elements that may form precipitates with carbon, fluorine, or phosphorus.

Missing elements are those that have been removed from the solution.

As a general rule, precipitations with ammonium sulphide are not attempted unless members of the Acid and Hydrogen Sulphide Groups have been removed, or are present in amounts that can be ignored. If these conditions are met, the addition of tartaric acid before the solution is made alkaline serves the very useful function of keeping members of the Ammonium Hydroxide Group, excepting iron, in solution (see Table 39). In the analysis of a clay, for example, such treatment permits a quantitative separation of iron from constituents such as aluminum, titanium, zirconium, vanadium, calcium, magnesium, and the alkalies. It should be noted, however, that although ammonium tartrate prevents the precipitation of phosphates such as those of aluminum and titanium, it does not prevent the precipitation of phosphates of the alkaline earths. Therefore, these can be expected to accompany iron if the original material contains phosphorus and the alkaline earths, and no preliminary separations of the two have been made. Similar considerations hold with carbon and fluorine, which form insoluble carbonates and fluorides with certain alkaline earths.

CHAPTER XI

SEPARATION OF THE AMMONIUM OXALATE GROUP

A. Elements That Are Precipitated by Ammonium Oxalate in Alkaline Solutions from Which the Members of the Acid, Hydrogen Sulphide, Ammonium Hydroxide, and Ammonium Sulphide Groups Have Been Removed

The elements that may be left in solution after separations of the Acid, Hydrogen Sulphide, Ammonium Hydroxide, and Ammonium Sulphide Groups in the General Procedure (page 35) are the alkaline earths, magnesium, the alkalies, and more or less of elements such as vanadium and tungsten that do not by themselves react with the group reagents. The next step in the analysis consists in precipitating the two members, calcium and strontium, of the Ammonium Oxalate Group. Such precipitations are made by (1) acidifying the filtrate and washings obtained in the separation of the Ammonium Sulphide Group (page 59); (2) adding ammonium oxalate or oxalic acid; (3) heating the clear solution to boiling; (4) stirring the solution and slowly adding diluted ammonium hydroxide until the solution is slightly alkaline; and (5) allowing the solution to stand for a while. The solution is then filtered and the precipitate washed moderately with a dilute solution of ammonium oxalate. The filtrate and washings are reserved for the precipitation of the Ammonium Phosphate Group (page 68).

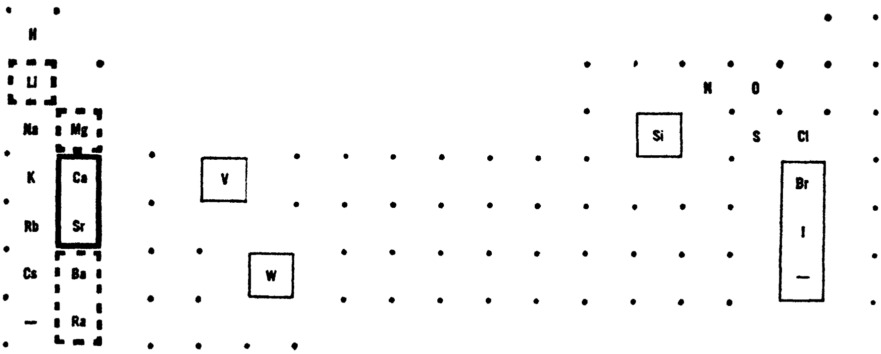
In the usual case, calcium alone is present, and its amount is determined by either igniting the precipitate, $CaC_2O_4 \cdot H_2O$, and weighing the resultant oxide, CaO, or by washing the precipitate with water to remove adhering ammonium oxalate, dissolving it in diluted sulphuric acid, and titrating the liberated oxalic acid with a standard solution of potassium permanganate.

Elements that must be considered in such treatments are shown in Table 40. Precipitation of calcium is never quite complete; the amount which remains in solution should not, however, exceed a few tenths of a milligram if operations have been carefully performed. Strontium is precipitated almost quantitatively. When it is present, determinations are made by igniting the precipitate, weighing the mixed oxides, and then determining and deducting the amount of strontium oxide. Coprecipitation of lithium, magnesium, and barium (in the absence of phosphate or carbonate ion) is slight in the usual analysis, and is overcome by dissolving the washed precipitate in hydrochloric acid and reprecipitating. Contamination by these elements cannot be cured by double precipitation in alkaline solution if phosphates are present. The same is true of lithium and barium in the presence of carbonates. It should be noted, however, that there is no difficulty in separating calcium from phosphates or carbonates by double precipitation as the oxalate if other precipitable elements are absent.

TABLE 40

Members of the Ammonium Oxalate Group

Elements that are precipitated by ammonium oxalate in an ammoniacal solution from which boron, carbon, fluorine, and the members of the Acid (page 43), Hydrogen Sulphide (page 53), Ammonium Hydroxide (page 56), and Ammonium Sulphide (page 60) Groups have been removed



Heavy solid blocks inclose members of the Ammonium Oxalate Group.

Heavy broken blocks inclose elements that may be present and may interfere by coprecipitation.

Light blocks inclose elements that are left in solution only under exceptional conditions.

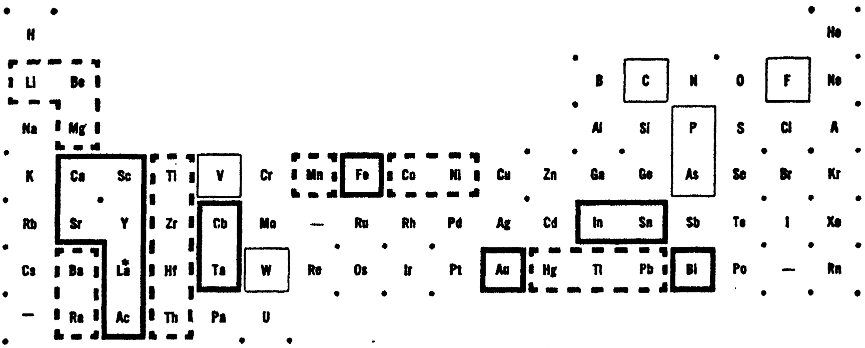
Missing elements are those that have been removed in the General Procedure.

B. Elements That Are Precipitated by Ammonium Oxalate in Alkaline Solutions from Which No Elements Have Been Removed

It is seldom indeed that calcium can be determined by direct precipitation with ammonium oxalate in an ammoniacal solution from which no elements have been removed. This follows, of course, because so many elements form precipitates under these conditions (see Table 41) that solutions of pure calcium salts are practically the only ones in which calcium is the only precipitable element. A goodly excess of ammonium hydroxide (*p*H 10) and ammonium chloride (5 g per 100 ml of solution) leads to less coprecipitation of elements such as manganese, cobalt, and nickel, and is desirable in separations involving copper, silver, zinc, and cadmium. These conditions slightly increase the amount of calcium and strontium left in solution. Aluminum is not precipitated if present in moderate amount in feebly ammoniacal solutions, but is almost completely precipitated in strongly ammoniacal solutions.

TABLE 41

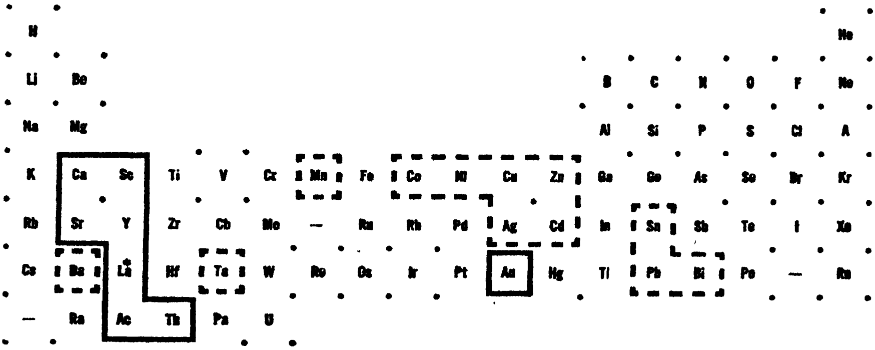
Elements That May Be Found in Precipitates Obtained by Adding Ammonium Oxalate to Feebly Alkaline Solutions (pH 8) from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks inclose elements that are precipitated completely or nearly so.
Heavy broken blocks inclose elements that are incompletely precipitated.
Light blocks inclose elements that may be precipitated under certain conditions.

TABLE 42

Elements That May Be Found in Precipitates Obtained by Adding Ammonium Oxalate to Feebly Acid Solutions (pH 3–4) from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose elements that are precipitated completely or nearly so.
Broken blocks inclose elements that are incompletely precipitated.

C. Elements That Are Precipitated by Ammonium Oxalate in Feebly Acid Solutions (*p*H 3–4) from Which No Elements Have Been Removed

It is sometimes desirable to determine calcium without first separating elements, such as iron, titanium, or phosphorus associated with magnesium, that form precipitates in alkaline solution. In such circumstances precipitations are made in solutions that contain as high a concentration of hydrogen ions as will permit reasonably complete precipitation of calcium oxalate. The proper acidity is usually established by the aid of an indicator, such as brom phenol blue, that changes color at the desired *p*H (3–4). Elements that are precipitated under such conditions are shown in Table 42. It will be noted that fewer elements are precipitated in acid than in alkaline solution (Table 41). Of the interfering elements, manganese is most frequently encountered. The procedure is especially desirable in the separation of calcium from large amounts of phosphorus, such as occur in phosphate rock.

CHAPTER XII

SEPARATION OF THE AMMONIUM PHOSPHATE GROUP

A. Elements That Are Precipitated by Diammonium Phosphate in Alkaline Solutions from Which the Members of the Acid, Hydrogen Sulphide, Ammonium Hydroxide, Ammonium Sulphide, and Ammonium Oxalate Groups Have Been Removed

In the General Procedure very few elements are left in solution after the orderly removal of the members of the Acid, Hydrogen Sulphide, Ammonium Hydroxide, Ammonium Sulphide, and Ammonium Oxalate Groups. The next, and as a rule the final, treatment consists in adding an excess of diammonium phosphate to the alkaline filtrate that is left after the separation of the Ammonium Oxalate Group (page 64), rendering the solution distinctly alkaline with ammonium hydroxide, and letting it stand for some time, usually overnight. Precipitates thus obtained are impure and of indefinite composition, and are usually separated by filtration, dissolved in diluted hydrochloric acid, and reprecipitated by adding a small amount of the phosphate reagent, rendering the solution alkaline and letting it stand for at least four hours. The solution is then filtered, and the precipitate is washed with diluted ammonium hydroxide, carefully ignited, and weighed.

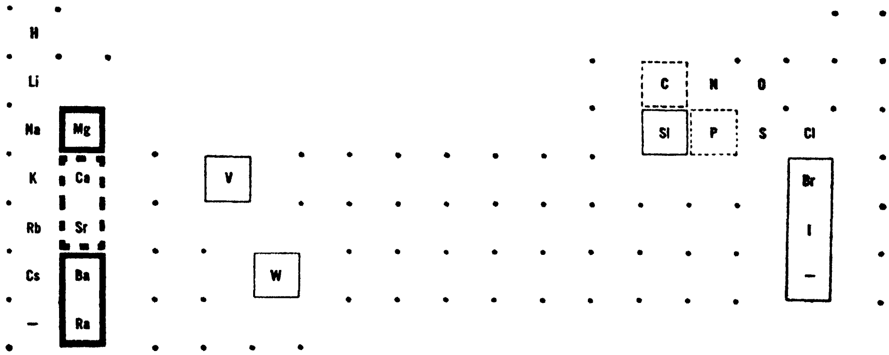
As shown in Table 43, these treatments serve for the precipitation of magnesium and barium together with such small amounts of calcium and strontium as may have escaped precipitation by ammonium oxalate. No more than 0.1 mg of magnesium should remain in solution in any event. Precipitation of barium is not complete, and very little if any will be found in the precipitate if only a few milligrams were originally present and double precipitations have been made. If the original material contains manganese, and the separation of the Ammonium Sulphide Group has been omitted, most of this element will be found here as well. Of these elements, magnesium and manganese yield definite compounds, $Mg_2P_2O_7$ and $Mn_2P_2O_7$, on ignition. Calcium and barium yield mixtures of the normal phosphates, $Ca_3(PO_4)_2$ and $Ba_3(PO_4)_2$, and pyrophosphates, $Ca_2P_2O_7$ and $Ba_2P_2O_7$. In careful analyses the ignited precipitate is tested for these elements, and proper corrections are made if they are found. Corrections for calcium and barium are made on the basis of the normal phosphates if their amounts are small, as they usually are. If large amounts are present, the corrections are too uncertain, and the elements must be removed before the magnesium is precipitated.

Radium is also precipitated, but its occurrence is so rare that its effect need not be considered. Significant amounts of barium and strontium are also rarely encountered, and the analyst has usually to deal only with magnesium, manganese, and calcium.

TABLE 43

Members of the Ammonium Phosphate Group

Elements that are precipitated by diammonium phosphate in ammoniacal solution after the removal of boron, carbon, fluorine, and the Acid (page 42), Hydrogen Sulphide (page 53), Ammonium Hydroxide (page 55), Ammonium Sulphide (page 59), and Ammonium Oxalate (page 64) Groups



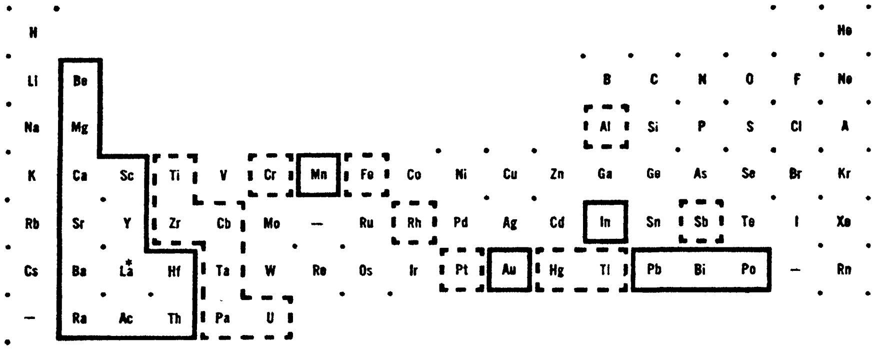
Heavy solid blocks inclose members of the Ammonium Phosphate Group.
Heavy broken blocks inclose elements which may not be completely precipitated by ammonium oxalate and which are then precipitated at this point.
Light solid blocks inclose elements left in solution only under exceptional conditions.
Light broken blocks inclose reintroduced elements.
Missing elements are those that have been removed in the General Procedure.

B. Elements That Are Precipitated by Diammonium Phosphate in Alkaline Solutions from Which No Elements Have Been Removed

Precipitations with diammonium phosphate in alkaline solutions from which no elements have been removed seldom serve a useful purpose, for a considerable number of elements form precipitates under these conditions. These are shown in Table 44, which emphasizes the fact that such precipitations are practically confined to solutions of pure magnesium or manganese salts. Of the elements that are precipitated, it might be remarked (1) that precipitations of indium, gold, strontium, and barium may not be quite complete, (2) that thallium is partially precipitated when trivalent and not precipitated when univalent, and (3) that it is assumed that the reactions of radium, actinium, scandium, yttrium, lanthanum, hafnium, protoactinium, and polonium take place as indicated. If present in high concentrations, certain of the other elements may also be partially precipitated.

TABLE 44

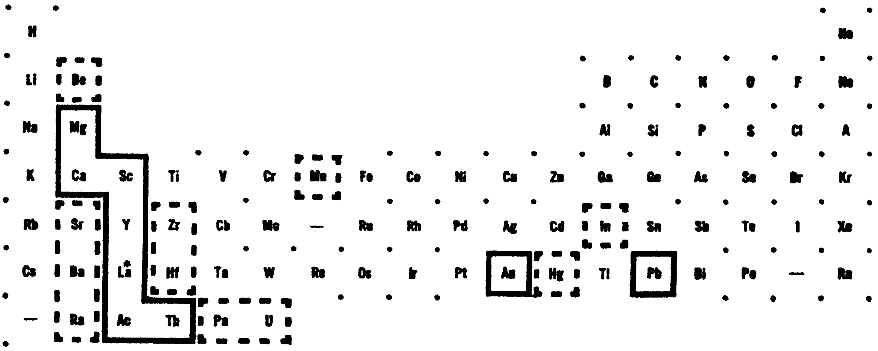
Elements That May Be Found in Precipitates Obtained by Adding Ammonium Phosphate to Ammoniacal Solutions (1 + 20) from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose elements that are precipitated completely or nearly so.
Broken blocks inclose elements that are incompletely precipitated.

TABLE 45

Elements That May Be Found in Precipitates Obtained by Adding Ammonium Phosphate to Ammoniacal Solutions (1 + 20) Containing Organic Compounds such as Citrates or Tartrates


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose completely precipitated elements.
Broken blocks inclose incompletely precipitated elements.

C. Elements That Are Precipitated by Diammonium Phosphate in Alkaline Solutions Containing Organic Compounds Such as Citrates or Tartrates

Precipitation of a number of elements by diammonium phosphate in ammoniacal solutions can be prevented by the use of certain organic compounds, such as citrates or tartrates. Such precipitations are usually made by starting with an acid solution, and then adding in turn citric or tartaric acid, an excess of diammonium phosphate, and enough ammonium hydroxide to render the solution distinctly alkaline. Elements that are precipitated under such conditions are shown in Table 45. It will be noted that the treatment does not prevent precipitation of elements such as the alkaline earths or manganese, and that determinations of magnesium by the procedure cannot be made unless the original material is free from the interfering elements, or they have been removed by appropriate treatments. As in B, it is assumed that the reactions of the uncommon elements radium, scandium, yttrium, lanthanum, the rare earths, hafnium, and polonium will take place as indicated.

CHAPTER XIII

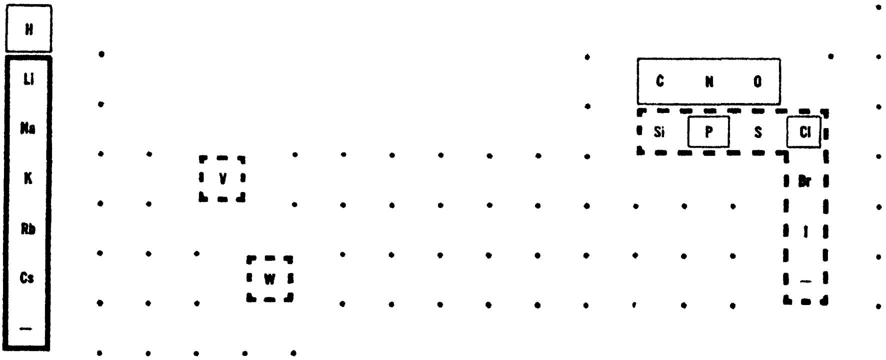
ELEMENTS THAT ARE NOT ADEQUATELY COVERED IN THE GENERAL PROCEDURE

A. Elements That May Be Left in Solution at the Conclusion of the General Procedure

The treatments employed for the removal of the members of the Acid, Hydrogen Sulphide, Ammonium Hydroxide, Ammonium Sulphide, Ammonium Oxalate, and Ammonium Phosphate Groups in the General Procedure of analysis may leave a number of elements still in solution. These are shown in Table 46. The alkalies are the only elements that are likely to survive the group separations quantitatively, for they do not respond to any of the group treatments, and are not carried down to any extent by the group precipitates, particularly if double precipitations are made. Nevertheless, determinations of the alkalies are usually made on separate samples (see the J. Lawrence Smith method, page 75), for it would be imperative to remove the excess of phosphate that was added in the precipitation of the Ammonium Phosphate Group, and this is no easy matter. In addition,

TABLE 46

Elements That May Be Left in Solution at the Conclusion of the General Procedure



Heavy blocks inclose elements originally present in the sample, which are left in solution.
Heavy broken blocks inclose elements originally present in the sample, which may still be present if certain conditions have prevailed.
Light blocks inclose elements introduced during the analysis.
Missing elements are those that are removed in the General Procedure.

foreign alkali salts are often introduced in the course of the analysis, either intentionally through fusions with alkali salts, or unintentionally through impurities in the reagents.

None of the other elements that may still be left in solution is apt to have quantitatively survived the group separations. For example, very little if any silicon, tungsten, or vanadium may remain, for silicon, tungsten, and, under some conditions, vanadium are caught in the Acid Group, and that which remains of these is likely to be carried down with the Ammonium Hydroxide Group, especially if the precipitate is large. Phosphorus will be present in quantity as a result of its use for the precipitation of the Ammonium Phosphate Group; none of the phosphorus originally present in the sample will remain in a well-ordered analysis. The amount of sulphur that will remain in solution depends entirely on the conditions that have obtained, all of it being left if it was originally present as sulphate in material that is free from elements, such as barium or strontium, that form insoluble sulphates; some, if not all of it, will have been lost or removed if the material contained volatile sulphur compounds such as sulphides or sulphites, or sulphates associated with elements such as barium. Hydrobromic and hydriodic acids are not easily expelled by evaporating solutions of their salts in hydrochloric acid; therefore small amounts of these elements may remain on the comparatively rare occasions on which they occur in the material under test. The remaining elements are present in abundance, hydrogen and oxygen being present in the water and reagents, carbon in the oxalate which was added, nitrogen in the ammonium hydroxide and ammonium salts, and chlorine as ammonium chloride and chlorides of the alkalies.

Finally, it should be noted that the solution may contain amounts ranging from a tenth to a few milligrams of the elements that are precipitated incompletely or with difficulty by their respective group reagents. Among these may be mentioned rhenium, germanium, platinum, iridium, nickel, strontium, and barium.

B. Elements That Are Not Caught in the General Procedure If They Occur Alone

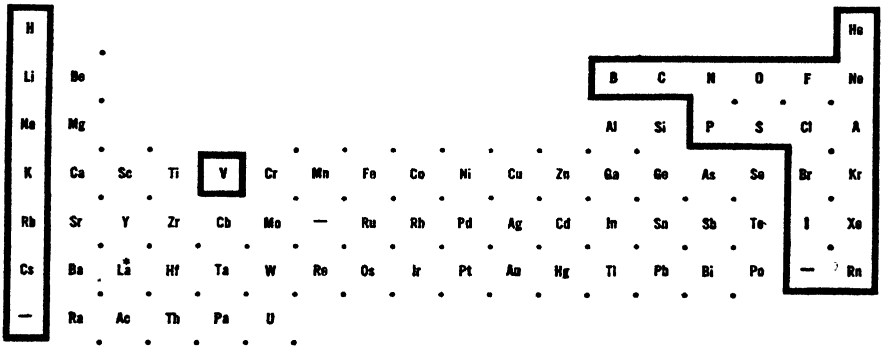
Elements that are not caught in the General Procedure if they occur alone are shown in Table 47. Of these, the alkalies give no indication of their presence throughout the analysis save the formation of a residue during the dehydration of the Acid Group; even this observation is impossible if a non-volatile compound was used in decomposing the material. Vanadium, if present in appreciable amount, would be betrayed (1) by the yellow color of the hydrochloric acid solution at the start of the analysis, (2) by the blue color that it would impart to the hydrochloric acid solution left after the separation of the Acid and Hydrogen Sulphide Groups, (3) by the characteristic color which it imparts to the filtrate of the Ammonium

Sulphide Group, and (4) by the brown precipitate that it yields when this solution is acidified. The gaseous elements are, of course, evolved and lost at the start of the analysis. The behavior of the acid-forming elements depends on the forms in which they occur. Volatile acids such as hydrobromic acid may be entirely lost during the solution of the material and the separation of the Acid Group. Non-volatile acids may remain in the free state or in combination with bases.

In addition to the elements shown in Table 47 there should be mentioned certain other elements that may escape observation in spite of the fact that they react with the reagents used in the General Procedure. These are the elements that form volatile compounds in acid solutions (see Table 14, page 29), and include germanium (quadrivalent), arsenic (trivalent), silicon, selenium, tellurium, antimony, tin, mercury, osmium, ruthenium, and rhenium. Germanium^{IV} and arsenic^{III} are readily volatilized, and are lost completely if hydrochloric acid solutions are boiled, or even evaporated to dryness on the steambath as in the separation of the Acid Group. Losses of the others may be serious, but are seldom complete unless special conditions prevail, as when (1) small amounts of silicon are accompanied by relatively large amounts of fluorine; (2) soluble selenides or tellurides are dissolved in a non-oxidizing acid at the start of the analysis; (3) selenium, tellurium, antimony, tin, or mercury is present in very small amount and treatment with hydrochloric acid has been vigorous; (4) osmium, ruthenium, and rhenium are subjected to rigorous treatment with an oxidant such as nitric or perchloric acid; and (5) sulphuric or perchloric acid solutions of rhenium are heated until fumes appear.

TABLE 47

Elements That Are Not Caught in the General Procedure If They Occur Alone



* Also elements 58–71.

The elements inclosed in heavy blocks do not form precipitates with any of the reagents used in the separations of the groups, and are therefore not caught if they occur alone.

CHAPTER XIV

SEPARATION OF THE ALKALI GROUP

In the J. Lawrence Smith method for the determination of the members of the Alkali Group in oxidized material such as rocks, the alkalies are converted to chlorides by intimately mixing the finely ground sample with ammonium chloride and calcium carbonate, and gradually heating to 1000–1200°C in a special-form platinum crucible which is tightly covered and kept relatively cool in the upper portion. The sintered mass is then extracted with water, whereby the alkali chlorides, together with other soluble compounds, such as calcium chloride and a large amount of calcium hydroxide, are dissolved. Elements such as silicon, iron, aluminum, magnesium, and beryllium remain in the residue as insoluble compounds formed during sintering, or by reaction with calcium hydroxide during the solution of the sintered mass. In the simplest case, the alkali chlorides are contaminated only by calcium chloride and calcium hydroxide. These are removed by successive treatments with ammonium carbonate and ammonium oxalate, followed by evaporation and gentle ignition to remove the ammonium salts that are thus introduced.

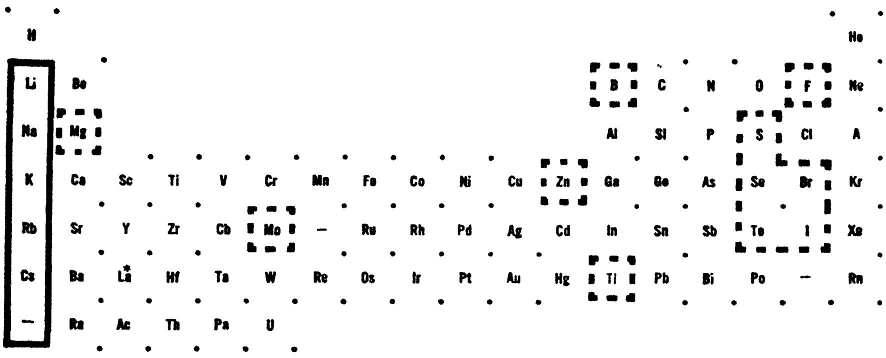
Of the alkalies, only sodium and potassium are usually encountered, and the percentages of each are obtained by (1) weighing the mixed chlorides; (2) precipitating potassium as the chloroplatinate, K_2PtCl_6, or the perchlorate, $KClO_4$, in alcoholic solution; (3) weighing the precipitate; (4) calculating the amount of potassium; and (5) calculating the percentage of sodium by difference.

Special treatments are required if lithium, rubidium, or cesium is present. If the material contains lithium, some of it remains in the extracted residue unless special treatments are introduced, some of it is carried down in the carbonate and oxalate precipitates, and the rest is weighed with the mixed chlorides. If it is ignored, it causes high results for sodium because lithium does not form an insoluble chloroplatinate or perchlorate. If no provision is made for rubidium and cesium (also the NH_4 ion), they are quantitatively gathered with the mixed chlorides and are counted as potassium, for they form insoluble chloroplatinates and perchlorates.

Other elements that will contaminate the mixed chlorides, if no special treatments are introduced when they are present in the material under test, are shown in Table 48. Of these, the commonest difficulties are caused by sulphates, which escape separation and finally combine with the alkalies to form sulphates. These weigh more per unit of alkali than chlorides do, and cause high results, for calculations are based on the assumption that the alkalies are present only as chlorides. In addition, sulphates cause high results for potassium, because sodium sulphate is much less soluble in alcohol than the chloride is, and it contaminates potassium chloroplatinate or perchlorate precipitates. Sulphates are therefore removed by adding barium chloride after most of the calcium has been removed, filtering, and then removing the excess of barium by treating with ammonium carbonate and again filtering. Magnesium interferes only if it is present in large amount and the insoluble residue is washed excessively. The remedy lies in keeping the washing solution always saturated with calcium hydroxide. Very little fluorine remains with the alkalies in the usual separations, and this can easily be removed by evaporating the mixed chlorides

TABLE 48

Elements That Are Caught or That Interfere in the J. Lawrence Smith Method for the Determination of Alkalies



* Also elements 58–71.
Solid blocks inclose elements that can be quantitatively caught.
Broken blocks inclose elements that may accompany the alkalies and cause errors.

two or three times with small portions of diluted hydrochloric acid (1 + 1) in platinum. Appreciable amounts of boron, on the other hand, escape separation and must be removed as the volatile ester by treating the mixed chlorides with diluted hydrochloric acid and methyl alcohol and then cautiously evaporating to dryness. The other elements that interfere are also removed by special treatments of the mixed chlorides, on the comparatively rare occasions when they are encountered. Thus bromine and iodine are removed by evaporating with diluted hydrochloric acid and hydrogen peroxide in porcelain (not platinum) and taking care to avoid loss by effervescence. Interference by zinc (which is slight), thallium (which is serious when it is univalent), or molybdenum (which is always serious) is avoided by precipitating them as sulphides before the chlorides are weighed, zinc and thallium by the use of freshly prepared ammonium sulphide in ammoniacal solution, and molybdenum by the use of hydrogen sulphide in dilute hydrochloric acid solution. After these treatments, the weighed chlorides must be tested for any sulphate that may have been formed. Selenium interferes in either valence; tellurium only when it is quadrivalent. These are removed by the use of sulphurous acid in dilute hydrochloric acid solution, followed by treatment to remove the sulphuric acid that results.

It might be noted at this point that determinations of the alkalies can be made by other procedures, such as Hicks' method for potassium (also cesium, rubidium, and the ammonium ion), or the triple acetate method for sodium. In the former, the amount of potassium is calculated after dissolving the chloroplatinate precipitate in acid, and determining its platinum content by reducing with magnesium, filtering, igniting, and weighing. The method can be applied in the presence of practically all the elements, for it is obvious that foreign compounds, such as sodium sulphate, in the chloroplatinate precipitate are of no moment so long as they contain no platinum or yield no insoluble compound in the reduction.

The triple acetate method is based on the formation of the fairly insoluble salt, $NaZn(UO_2)_3(CH_3COO)_9 \cdot 6\,H_2O$ or $NaMg(UO_2)_3(CH_3COO)_9 \cdot 6\,H_2O$, under carefully controlled temperature and concentration. This method is also of quite general application, the chief interfering substances being lithium, strontium, phosphate ion, sulphate ion in the presence of potassium, and certain organic acids.

II. SPECIAL PROCEDURES FOR SEPARATING THE ELEMENTS

CHAPTER XV

SEPARATION OF MEMBERS OF THE HYDROGEN SULPHIDE GROUP FROM ONE ANOTHER

A. Separations within the Hydrogen Sulphide Group Based on Adjustment of the Acidity of the Solution

Separations of members of the Hydrogen Sulphide Group from one another by precipitating with hydrogen sulphide in solutions of adjusted acidity are not as successful as might be expected from the data shown in Table 33 because some sulphides tend to carry down other sulphides. Conditions can be adjusted, however, so that certain separations can be made, as for example arsenic from antimony, copper or bismuth from cadmium, or most of the members of the group from other sulphide-forming elements such as thallium or zinc.

B. Separations within the Hydrogen Sulphide Group Based on Digestion with a Solution of an Alkaline Sulphide

The members of the Hydrogen Sulphide Group whose sulphides are insoluble in ammonium polysulphide, $(NH_4)_2S_x$, comprise the Copper Group; those whose sulphides are soluble comprise the Arsenic Group.[1] The sulphides of a few members of the Hydrogen Sulphide Group are partially soluble, and these can therefore be expected in both subgroups. The distribution of the members of the Hydrogen Sulphide Group in the two subgroups is shown in Tables 49 and 50. In qualitative analyses, the groups are usually separated by digesting the sulphides in a warm solution of an alkaline sulphide and then filtering. In quantitative analyses the separation is often made by pouring a feebly acid solution of the elements into a warm solution containing an excess of the alkaline sulphide, digesting for a while, and filtering, or (if all or nearly all of the elements are soluble in an alkaline solution) by treating the alkaline solution of the elements with the alkali sulphide. Such treatments usually yield better separations of

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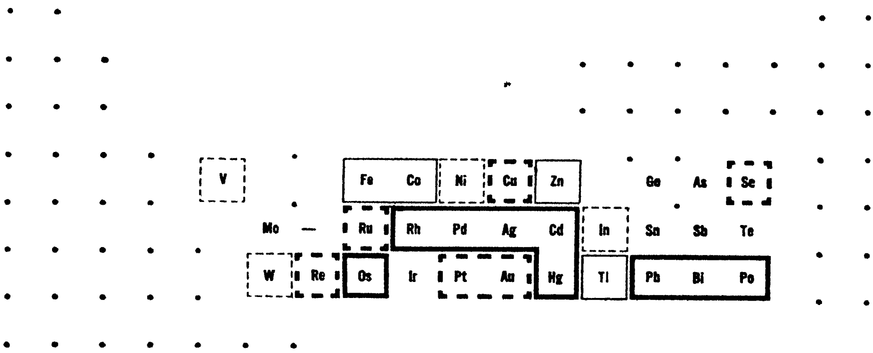
[1] The Arsenic Group is sometimes called the Tin Group, and occasionally the groups are called A or B depending on which is examined first after the separation. It will be noted that copper is slightly soluble in $(NH_4)_2S_x$ and will be found in small part in the Arsenic Group.

TABLE 49

Members of the Copper Subgroup of the Hydrogen Sulphide Group



Heavy blocks inclose members of the Hydrogen Sulphide Group (see Table 34, page 54) whose sulphides are insoluble in $(NH_4)_2S_x$ (Copper Group).

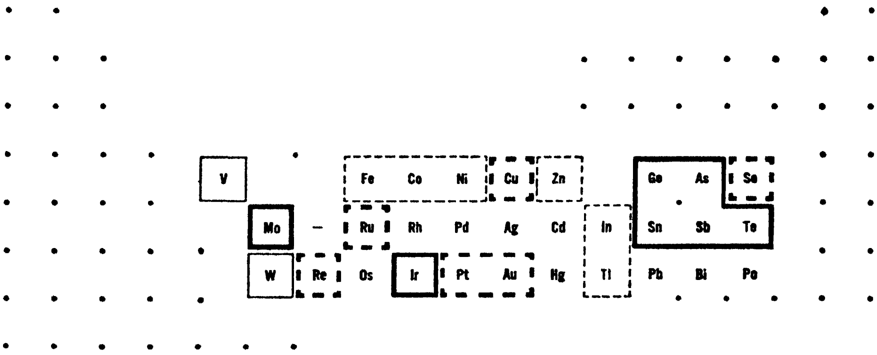
Heavy broken blocks inclose members of the Hydrogen Sulphide Group whose sulphides are partially soluble in $(NH_4)_2S_x$.

Light blocks inclose contaminants of the Hydrogen Sulphide Group whose sulphides are insoluble in $(NH_4)_2S_x$.

Light broken blocks inclose contaminants of the Hydrogen Sulphide Group whose sulphides are soluble (V and W) or partially soluble (Ni, In) in $(NH_4)_2S_x$.

TABLE 50

Members of the Arsenic Subgroup of the Hydrogen Sulphide Group



Heavy blocks inclose members of the Hydrogen Sulphide Group (see Table 34, page 54) whose sulphides are soluble in $(NH_4)_2S_x$ (Arsenic Group).

Heavy broken blocks inclose members of the group whose sulphides are partially soluble in $(NH_4)_2S_x$.

Light blocks inclose contaminants of the group whose sulphides are soluble in $(NH_4)_2S_x$.

Light broken blocks inclose contaminants of the group whose sulphides are insoluble (Fe, Co, Zn, Tl) or sparingly soluble (Ni, In).

members of the Arsenic Group from members of the Copper Group than can be obtained by digesting the sulphides. Even so, the separations are not always perfect, particularly those involving ruthenium, platinum, gold, selenium, and, if ammonium polysulphide is used, copper. For this reason digestions with alkaline sulphides are used more often in qualitative than in quantitative analyses.

If the alkaline sulphide is added in excess to solutions from which no elements have been removed, the insoluble residue will, of course, contain any element, such as zinc, thallium, iron, or chromium, that reacts with alkali sulphide to form an insoluble precipitate.

It should be noted that the distribution of the elements in the two subgroups may be changed if an alkaline solution other than ammonium polysulphide is used. Thus, mercury and more or less bismuth will be found in the Arsenic instead of the Copper Group if a solution of sodium hydroxide and sodium sulphide is substituted for ammonium polysulphide. Similarly, most of the rhenium will be found in the Arsenic Group if a solution of ammonium polysulphide is used, while all of it will be found in the Copper Group if a solution of primary ammonium sulphide, NH_4HS, is substituted for ammonium polysulphide and the solution is allowed to stand for one or two days.

C. Separations within the Hydrogen Sulphide Group Based on the Formation of a Complex Ion

Certain members of the Hydrogen Sulphide Group can enter into complex anions which do not react with hydrogen sulphide. This is true of copper, which reacts with cyanide in alkaline solutions to form a complex anion; of tin, which forms complex anions with oxalic or hydrofluoric acids; and of germanium, which forms a complex anion with hydrofluoric acid. These reactions serve for the separation of members of the Hydrogen Sulphide Group that enter into the complex anions from those that do not.

Ammonium chloride tends to prevent the complete precipitation of lead, cadmium, and quadrivalent tin in dilute acid solution.

CHAPTER XVI

SEPARATIONS OF MEMBERS OF THE AMMONIUM HYDROXIDE GROUP FROM ONE ANOTHER

A. Separations within the Ammonium Hydroxide Group Based on Precipitation with Sodium Hydroxide

Precipitations by sodium hydroxide are usually made by treating an acid solution of the elements with sodium hydroxide until most of the acid has been neutralized, warming, pouring the solution slowly and while stirring into a hot solution containing enough sodium hydroxide to yield a 5 per cent solution when mixed, boiling for 1 minute, and allowing the solution to cool for 15–30 minutes. The solution is then filtered through a filtering crucible, or filter paper that has been washed with a 5 per cent solution of sodium hydroxide, and the precipitate is washed with a 1 per cent solution of the alkali, containing an electrolyte such as sodium sulphate. The precipitate is never weighed as such, but is dissolved, and the solution treated as the case may require.

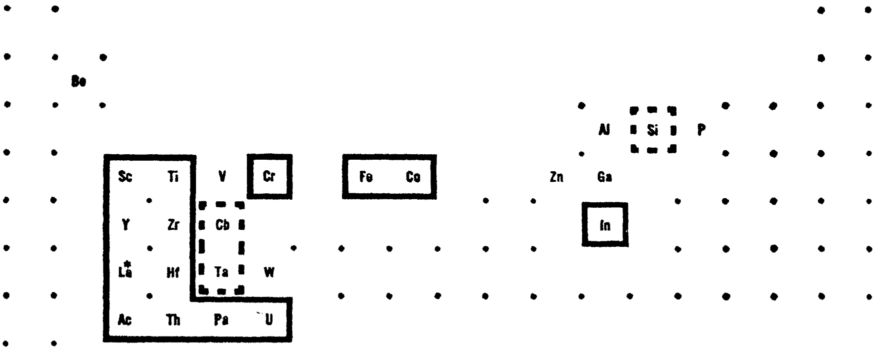
As a general rule, such precipitations are useful only after certain preliminary separations have been made as, for example, in a hydrochloric acid solution of the precipitate that is obtained with ammonium hydroxide in the course of the General Procedure (Table 35, page 56). The separations that can be expected in this case are illustrated in Table 51. It will be noted that one important use of the precipitation is to separate aluminum, and also beryllium and gallium, should they happen to be present, from iron and the other precipitable members of the Ammonium Hydroxide Group. If aluminum is to be determined in the filtrate, one of the drawbacks of the separation is that elements such as vanadium, tungsten, zinc, silicon, and phosphorus (that may have been carried down by the ammonium hydroxide precipitate), accompany aluminum in solution and render its determination more difficult. Traces of zirconium, titanium, and thorium tend to pass into the filtrate if no other precipitable elements are present; in the presence of a tenfold excess of trivalent iron precipitation is complete. Columbium and tantalum are incompletely precipitated when alone; better, though not complete, precipitation is obtained when iron is present.

It is also apparent that a precipitation with sodium hydroxide can serve to separate elements such as vanadium and phosphorus from elements such as iron and titanium. The separation of vanadium or phosphorus from cerium (and probably other members of the rare earth group), or of

TABLE 51

Separations within the Ammonium Hydroxide Group Based on Precipitations with Sodium Hydroxide

(Si, P, V, W, Co, and Zn may be present in the ammonium hydroxide precipitate although not precipitated when alone)



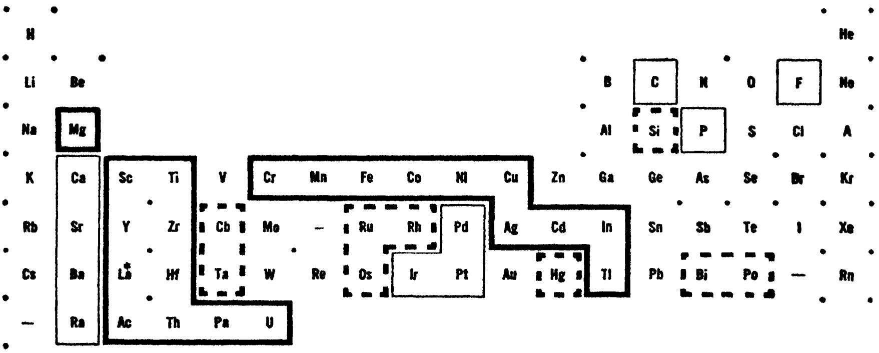
* Also elements 58–71.

Heavy solid blocks inclose elements of the Ammonium Hydroxide Group (see Table 35, page 56) that can be precipitated quantitatively by sodium hydroxide or very nearly so.

Heavy broken blocks inclose elements that are partially precipitated by sodium hydroxide.

TABLE 52

Elements That May Be Found in Precipitates Obtained by Adding Sodium Hydroxide to Solutions from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that are precipitated completely or nearly so.

Heavy broken blocks inclose elements that are incompletely precipitated.

Light solid blocks inclose elements that may interfere.

gallium from indium, is not so satisfactory. It should be noted that glass vessels are rapidly attacked when strong alkaline solutions are boiled in them and that operations must be carried through in platinum, or similar material, if the contamination is of moment.

Occasionally, precipitation with sodium hydroxide is employed in solutions from which no elements have been removed. The distribution of the elements in such cases is shown in Table 52. Precipitation made under such conditions can serve a useful purpose only under special circumstances as, for example, in the separation of molybdenum from iron.

In addition to the larger number of elements that can be expected in the precipitate and filtrate if no prior separations have been made, difficulties may be introduced if elements are present in certain combinations. For example, aluminum is precipitated in part if magnesium or nickel is present in the solution; iron is incompletely precipitated if certain compounds of carbon are present; zinc is carried down to some extent if much chromium or iron is present; and members of the alkaline earth group are precipitated, at least in part, as phosphates or fluorides in solutions containing appreciable amounts of these ions. The fluoride ion has little or no retarding effect on the precipitation of elements such as iron, nickel, silver, cadmium, indium, or zirconium. Considerable precipitation of gold and the six platinum metals may occur if other precipitable elements are present, or if the solution is allowed to stand for more than 30 minutes. Ordinarily, however, very little precipitation of gold, platinum, palladium, or iridium takes place if they occur alone and are present in small amount. Chromium is completely precipitated if it is in the trivalent state and the solution is boiled; no precipitate is formed in cold solution, or in either hot or cold solutions if it is in the sexivalent state. Thallium is completely precipitated when in the trivalent, and not at all when in the univalent, state. Antimony is not precipitated in either the trivalent or quinquevalent state. The precipitation of copper or indium may be incomplete if the concentration of sodium hydroxide exceeds 1 per cent.

B. Separations within the Ammonium Hydroxide Group Based on Precipitation with Sodium Hydroxide and Sodium Carbonate

Precipitations by sodium hydroxide and sodium carbonate are made as described under Precipitation by Sodium Hydroxide (page 81), excepting that 1–2 g of sodium carbonate is added per 100 ml of the sodium hydroxide solution. If precipitations are made in acid solutions of the ammonium hydroxide precipitate which is obtained in the course of the General Procedure (page 55), the results do not differ from those obtained with sodium hydroxide alone, except in the case of uranium which remains in solution. If precipitations are made without any preliminary separations, the results differ from those obtained with sodium hydroxide alone, for the number of elements that are caught in the precipitate is increased by the alkaline earths, which are precipitated as carbonates, and decreased by uranium which remains in solution. The reactions of the elements in such precipitations are shown in Table 53. The remarks under Precipitation by Sodium Hydroxide hold, in general, for this precipitation as well, except that there is less tendency for osmium to precipitate when carbonate is present.

Like treatment with sodium hydroxide under similar circumstances, the method has limited application.

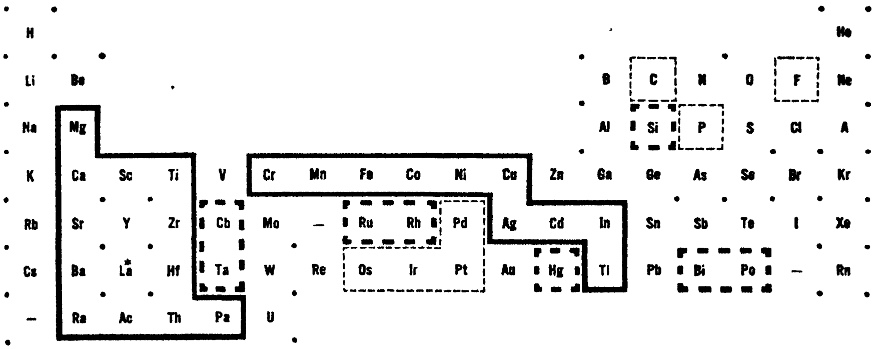
C. Separations within the Ammonium Hydroxide Group Based on Precipitation with Sodium Peroxide

Precipitations by sodium peroxide are made as described under Precipitation by Sodium Hydroxide (page 81), except that the nearly neutralized solution is poured into a cool solution of sodium peroxide, and it is necessary to boil the solution or to digest it on the steambath for at least 30 minutes before it is set aside to cool. The prolonged heating is necessary to insure complete precipitation of elements like titanium, which are at first partially converted to soluble oxidized compounds that are not broken up unless the solution is heated for some time. Sodium hydroxide containing hydrogen peroxide can, of course, be substituted for sodium peroxide. Better separations of uranium are obtained if sodium carbonate is added before the precipitation. As can be seen in Table 54, the net result of the treatment with sodium peroxide instead of sodium hydroxide is to add chromium and uranium to the elements that can be expected to accompany aluminum in the filtrate. Their oxidized compounds are yellow, and they can be determined in the filtrate by colorimetric methods if they occur singly and are present in small amount. The remarks made under Precipitation by Sodium Hydroxide (page 81) hold, in general, for this precipitation as well.

The above statements refer to precipitations made in a hydrochloric acid solution of the precipitate obtained with ammonium hydroxide in the course of an analysis by the General Procedure (Table 35, page 56). If precipitations are made in solutions from which no other elements have been removed, the results will differ from those obtained with sodium hydroxide under like conditions (Table 52) in that (1) uranium and chromium will be found in the filtrate as shown in Table 54; (2) mercury and gold will be precipitated as metal instead of the oxide; (3) trivalent thallium is only partially precipitated and univalent thallium is oxidized and partially precipitated; and (4) osmium and ruthenium show even less tendency toward precipitation.

TABLE 53

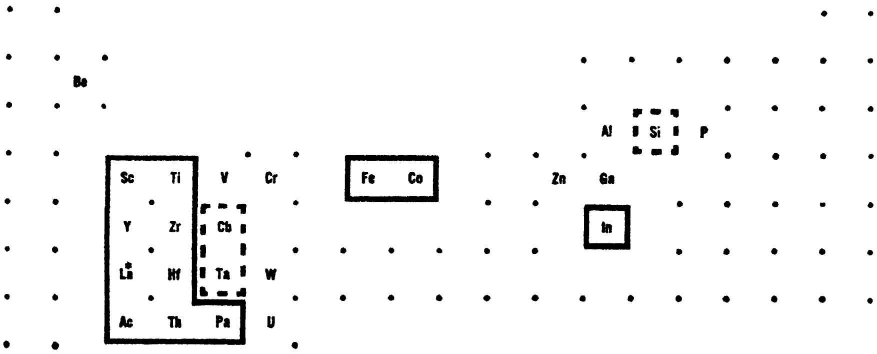
Elements That May Be Found in Precipitates Obtained by Adding Sodium Hydroxide and Sodium Carbonate to Solutions from Which No Elements Have Been Removed


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks inclose elements that are precipitated completely or very nearly so.
Heavy broken blocks inclose elements that are incompletely precipitated.
Light broken blocks inclose elements that may interfere under certain conditions.

TABLE 54

Elements That May Be Found in Precipitates Obtained by Adding Sodium Peroxide to an Acid Solution of the Ammonium Hydroxide Group Precipitate



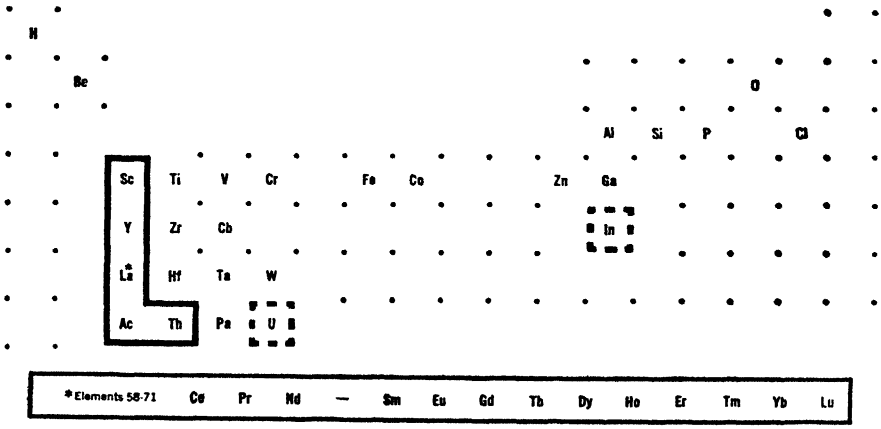
* Also elements 58–71.
Heavy solid blocks inclose elements of the Ammonium Hydroxide Group (see Table 35, page 56) that are precipitated quantitatively or very nearly so.
Heavy broken blocks inclose elements that are partially precipitated.

D. Separations within the Ammonium Hydroxide Group Based on Precipitation with Hydrofluoric Acid

Of the 32 elements that are normal components of an ammonium hydroxide precipitate which has been obtained in the General Procedure (Table 35), only the so-called rare earths form fluorides that are reasonably insoluble in dilute solutions containing hydrofluoric and hydrochloric acids. These, numbering 19 in all, are shown in Table 55. Uranium forms an insoluble fluoride only if quadrivalent. Indium is not precipitated when alone, but is carried down by certain rare earth fluorides. A few members of other groups, such as magnesium and calcium, also form insoluble fluorides, and so the precipitation is usually made after a preliminary separation of the Ammonium Hydroxide Group.

TABLE 55

Elements That May Be Found in Precipitates Obtained by Adding Hydrofluoric Acid to a Hydrochloric Acid Solution of the Ammonium Hydroxide Group Precipitate



Solid blocks inclose elements of the Ammonium Hydroxide Group (see Table 35, page 56) that are precipitated completely or nearly so.
Broken blocks inclose elements that are precipitated under certain conditions.

In such case, the ammonium hydroxide precipitate is dissolved in hydrochloric acid, the solution is evaporated nearly to dryness, treated with hydrofluoric acid, and evaporated on the steambath until dry. The residue is then moistened with 0.5 ml of hydrofluoric acid, treated with 25 ml of water containing 0.5 ml of hydrochloric acid, digested for a few minutes, filtered, and washed with water containing 1 ml each of the two acids per 100 ml. All operations must, of course, be performed in materials, such as platinum dishes and hard-rubber funnels, that are not attacked by hydrofluoric acid.

Precipitation with hydrofluoric acid serves only as a separation, for the fluorides are usually impure and cannot be weighed as such. Determinations of the rare earths are usually made by (1) decomposing the fluorides and expelling the hydrofluoric acid by treating with sulphuric acid and evaporating to fumes of the latter; (2) diluting, precipitating with ammonium hydroxide, and filtering; (3) dissolving the precipitate in diluted hydrochloric acid; and (4) precipitating with oxalic acid as described in the next section.

E. Separations within the Ammonium Hydroxide Group Based on Precipitation with Oxalic Acid

As has been stated in the preceding section, the rare earths are usually separated by precipitating with hydrofluoric acid, and then determined by precipitating with oxalic acid. So far as the precipitation of the rare earths is concerned, there is not much to choose between the two methods. The former, however, yields a much better separation of the rare earths from the other members of the Ammonium Hydroxide Group, and is therefore usually employed as a preliminary separation. Precipitation with oxalic acid then serves as an additional separation, and at the same time yields a precipitate that can be ignited and weighed. In general, precipitation is done by obtaining a solution of the rare earths in 0.5 *N* hydrochloric acid (less acid with actinium), boiling, stirring vigorously as a hot saturated solution of oxalic acid is added, and then allowing the solution to cool and stand overnight. The solution is then filtered; the precipitate is washed with a 1 per cent solution of oxalic acid and ignited to the oxides.

The ignited residue can be expected to contain the same elements, except uranium and possibly indium, as are precipitated by hydrofluoric acid (Table 55). It may also contain other elements if precipitation with oxalic acid is attempted before the members of the ammonium hydroxide group have been separated, for a number of elements, such as calcium, strontium, zinc, and cobalt, yield oxalates that are more or less insoluble.

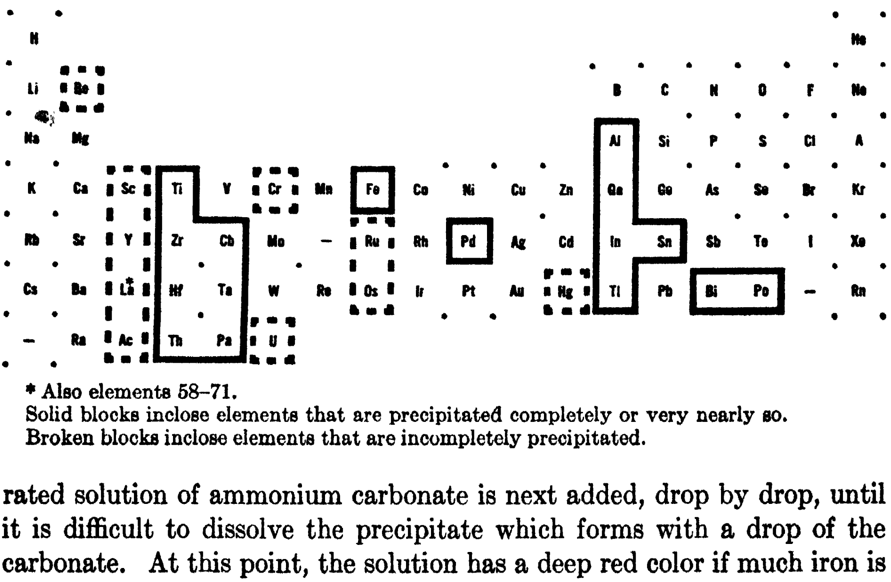
CHAPTER XVII

PRECIPITATION BY THE BASIC ACETATE METHOD

Precipitations by hydrolysis in solutions of acetic acid that are buffered by sodium acetate are usually made for the purpose of separating manganese, nickel, or zinc from elements such as iron and titanium. Directions for the precipitation vary, but usually oxidation of the iron to the trivalent state is made certain, and then most of the free acid is neutralized by adding diluted ammonium hydroxide slowly and while stirring vigorously. The volume of the solution is kept low, not over 100 ml, at this stage. A saturated solution of ammonium carbonate is next added, drop by drop, until it is difficult to dissolve the precipitate which forms with a drop of the carbonate. At this point, the solution has a deep red color if much iron is present, and the pH is about 2.5. The solution is now diluted to 400 ml, heated to boiling, treated with 15 ml of a 20 per cent solution of sodium acetate ($NaC_2H_3O_2 \cdot 3\ H_2O$), and the boiling continued for 3 minutes. After the precipitate has settled, the solution is filtered and the precipitate washed with hot water. The pH of the filtrate should be close to 5.6 if operations have been properly performed. In such a procedure, elements react as shown in Table 56 when they are by themselves.

TABLE 56

Precipitation by the Basic Acetate Method


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Solid blocks inclose elements that are precipitated completely or very nearly so.

Broken blocks inclose elements that are incompletely precipitated.

The precipitation of quadrivalent cerium is complete; that of trivalent cerium, incomplete. Little if any mercury is precipitated unless the solution is allowed to stand for some time. Trivalent thallium is completely precipitated, but univalent thallium is not precipitated at all.

If a ten- to twentyfold excess of iron as a ferric salt is present at the start, complete precipitation of silicon, trivalent antimony, quadrivalent selenium and tellurium, quinquevalent arsenic, antimony, vanadium, and phosphorus, and sexivalent selenium, tellurium, tungsten, and molybdenum can be obtained. This ratio of iron also causes precipitation of all but traces of germanium, quadrivalent vanadium, and trivalent arsenic; under such conditions about half of the lead is precipitated. Somewhat similar reactions would, of course, take place if elements such as aluminum or titanium were present instead of iron.

CHAPTER XVIII

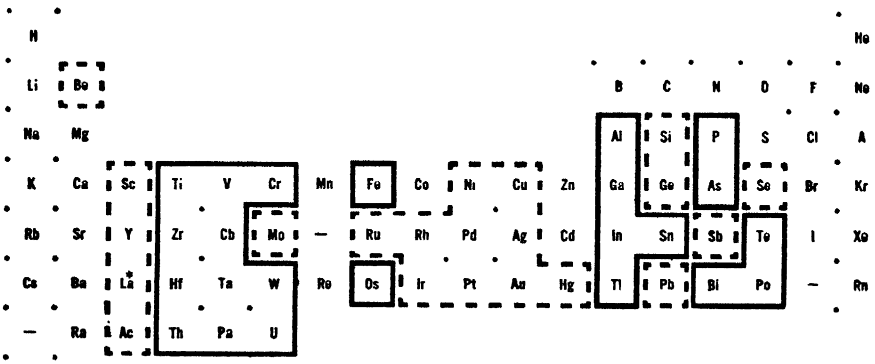
PRECIPITATION BY MEANS OF ZINC OXIDE

Precipitations with zinc oxide are usually made for the purpose of separating cobalt or manganese from accompanying elements such as trivalent iron or chromium. In such precipitations a suspension of the finely divided oxide (*p*H about 5.2) is added in excess to a slightly acid solution which, in the usual analysis, has first been subjected to a mild oxidizing treatment. For example, materials such as irons and steels are dissolved in hydrochloric or sulphuric acid and then treated with nitric acid. As a rule, precipitation is made at room temperature, the solution is allowed to stand for 15 to 30 minutes before filtration, and an aliquot portion of the filtrate is used for the determination of the element in question. Elements precipitated under such circumstances are shown in Table 57. Essentially the same reactions take place if precipitations are made at 100°C.

TABLE 57

Precipitation by Means of Zinc Oxide

(After oxidation with nitric acid)


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose elements that are completely precipitated, or very nearly so.
Broken blocks inclose elements that are incompletely precipitated.

The following observations are of interest: (1) Complete precipitation occurs with quadrivalent tin and with moderate amounts of bivalent tin, with trivalent thallium, quadrivalent tellurium, quinquevalent arsenic, quadrivalent or moderate amounts of quinquevalent vanadium, and with quadrivalent or moderate amounts of sexivalent uranium; (2) cerium is quantitatively precipitated if in the quadrivalent and not at all if in the trivalent state; as for scandium, yttrium, lanthanum, actinium, and the remaining rare earths, it is quite likely that a few, like lanthanum, are not precipitated at all, and that the others are precipitated more or less completely; (3) tungsten is quantitatively contained in the precipitate if converted to yellow tungstic acid before adding the zinc oxide, but is incompletely precipitated if it is not first oxidized; (4) copper and silicon are almost completely precipitated; (5) arsenic in the trivalent, selenium in the quadrivalent, and antimony in either the trivalent or quinquevalent states are partially precipitated; (6) nickel, lead, germanium, mercury, and silver are precipitated to such a slight extent that most if not all of them can be recovered by reprecipitation; (7) chromium in the sexivalent and thallium in the univalent state are not precipitated; (8) boron may be precipitated in part if large amounts of elements such as iron or aluminum are present, and fluorine may cause the retention of elements of the alkaline earths or rare earths group if these are present in large amounts. It should be noted that Sn^{II}, V^{V}, and U^{VI} are not completely precipitated unless zinc oxide is present in large excess and filtration is continued until a perfectly clear solution is obtained. Finally, it is quite possible that some of the elements that are incompletely precipitated when alone may be completely precipitated if another element, such as iron, predominates to a marked extent.

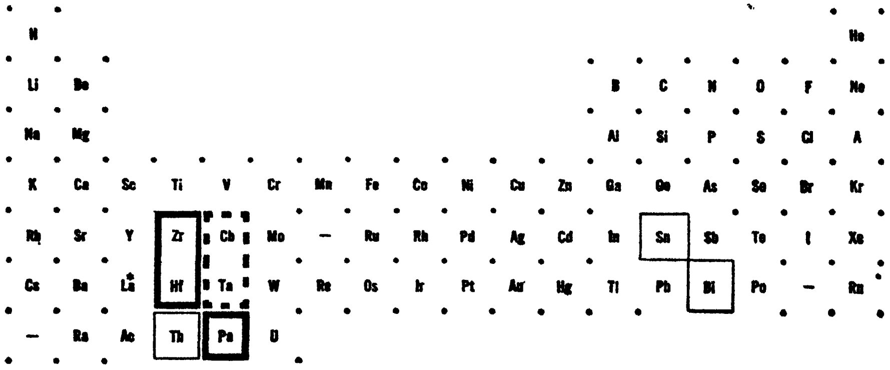
CHAPTER XIX

PRECIPITATION BY PHOSPHORIC ACID IN STRONG ACID SOLUTION

The number of elements that can be precipitated as phosphates grows progressively smaller as the hydrogen-ion concentration of the solution is increased until, in an acidity corresponding to that of diluted sulphuric acid (1 + 9), only four elements yield precipitates in clear solutions which do not contain unduly large concentrations of the other elements. If hydrogen peroxide is present, one of the four elements, titanium, also remains in solution, and so in general the reaction serves for the detection and determination of the remaining three, zirconium, hafnium, and protoactinium.

TABLE 58

Precipitation with Phosphoric Acid in Strongly Acid Solutions Containing Hydrogen Peroxide


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that are completely precipitated.

Heavy broken blocks inclose elements that are not precipitated when alone but are carried down by zirconium or hafnium.

Light blocks inclose elements that may be partially precipitated if present in considerable amount, but which can be removed by reprecipitation.

As a general rule, precipitations are made by adding diammonium phosphate or phosphoric acid to a diluted sulphuric acid solution (1 + 9) containing hydrogen peroxide, warming to about 40°C, and then allowing the solution to stand for several hours. Elements that form precipitates, or are most likely to interfere if precipitations are made without preliminary separations of any of the elements, are shown in Table 58. It is understood, of course, that another acid, such as hydrochloric, must be substituted for sulphuric acid if elements that form insoluble sulphates are present. As a matter of fact, precipitations are usually made in solutions of groups of elements that have first been separated by other procedures, such as by precipitation with ammonium hydroxide in the General Procedure (page 55), or with cupferron (page 117) in solutions from which the members of the Hydrogen Sulphide Group have been removed.

It has already been stated that titanium forms an insoluble phosphate if hydrogen peroxide is not present. Elements such as tin, bismuth, and thorium form precipitates in concentrated solutions of their salts, but no precipitation takes place in solutions of moderate concentration. Contamination of the zirconium, hafnium, or protoactinium precipitate by these elements can always be avoided by reprecipitating once or twice. Columbium and tantalum, on the other hand, are true interfering elements, for though they are not precipitated when alone, they are carried down in part by zirconium or hafnium phosphates, and cannot be completely separated by reprecipitation. Separations of these elements must, therefore, be made by other means on the comparatively rare occasions in which they occur together.

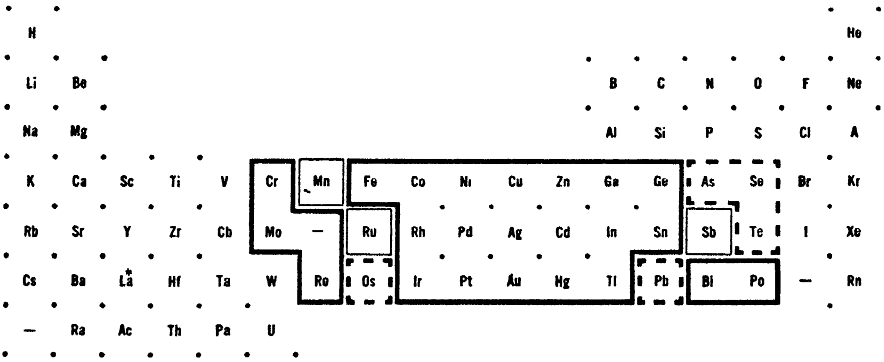
CHAPTER XX

ELECTROLYSIS WITH A MERCURY CATHODE

Electrolyses with a mercury cathode are always made in acid solutions. Elements that can be deposited in the mercury under such conditions are shown in Table 59. In quantitative determinations the mercury is, of course, weighed before and after the electrolysis. So many elements are deposited that the method finds very restricted application in *determinations* of the elements. It is, however, of considerable value for the *removal* of elements that are not wanted in a solution. Thus, in a determination of aluminum in steel, electrolysis with a mercury cathode in diluted sulphuric acid (less than 1 per cent by volume) solution serves for the removal of all the iron, as well as elements such as chromium, nickel, copper, tin, or molybdenum that may be present as impurities or as alloying constituents.

TABLE 59

Electrolysis with a Mercury Cathode in Dilute (approximately 0.3 *N*) Sulphuric Acid Solution


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71. (Partial deposition of La and Nd has been reported.)

Heavy solid blocks inclose elements that can be quantitatively deposited in the mercury cathode.

Heavy broken blocks inclose elements that are quantitatively separated from the electrolyte, but are not quantitatively deposited in the mercury.

Light blocks inclose elements that are incompletely separated.

Some of the elements that can be completely removed from the electrolyte are not quantitatively deposited in the mercury. Lead may be partially deposited on the anode, some arsenic is volatilized as arsine at the cathode, some osmium is volatilized as the tetroxide at the anode, and selenium and tellurium are reduced to the elemental state and remain suspended in the electrolyte, from which they can be removed by filtration. Iridium is completely deposited with difficulty. As for the elements that are incompletely separated from the electrolyte, ruthenium is incompletely deposited in the mercury and none is volatilized, manganese is incompletely deposited in the mercury and on the anode, and antimony is partly deposited in the mercury, and partly volatilized as stibine, at the cathode.

Because the deposited elements cannot be easily extracted from the mercury for the purpose of determination, they are allowed to remain in the mercury until it becomes so contaminated that purification is necessary.

CHAPTER XXI

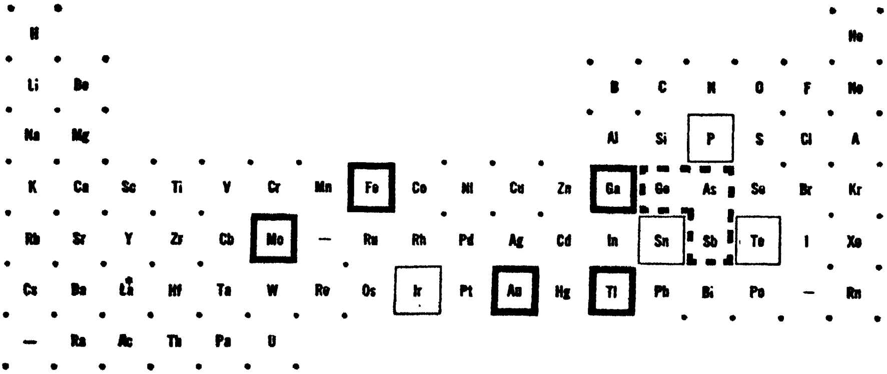
EXTRACTION WITH ETHER

A very useful method for the separation of certain elements from others is that in which a compound, usually a chloride dissolved in diluted hydrochloric acid, is extracted with ether. The approximate solubilities of certain chlorides are indicated in Table 60.

The conditions usually established can be illustrated by those required in separations of iron. These are (1) the conversion of the iron to ferric chloride; (2) solution of the ferric chloride in cold hydrochloric acid having a specific gravity of 1.10; (3) extraction of the ferric chloride by shaking with 1 to 3 portions of ether; and (4) the recovery of chlorides that may be entrapped in the ether by shaking the combined ether extracts with 1 to 3 portions of cold hydrochloric acid, specific gravity 1.10, that has first been saturated with ether. Single extractions suffice for certain purposes, but repeated extractions are needed for maximum separations. High concentrations of compounds, such as sodium chloride, which are insoluble in ether must be avoided.

TABLE 60

Extraction with Ether


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks represent more than 90 per cent extraction.
Heavy broken blocks represent from 50 to 90 per cent extraction.
Light blocks represent from 1 to 50 per cent extraction.

Extraction with ether is very often used if iron occurs in such large amount that it interferes in determinations of accompanying elements. The extraction of iron is never complete, but, with proper precautions and repeated treatments, no more than a few tenths of a milligram need be left in the hydrochloric acid solution.

As for the other elements, molybdenum must be in the sexivalent state, and better extractions are obtained if it is associated with ferric chloride. Under such conditions all but a tenth of a milligram or so can be extracted. Extractions of gold, thallium, and gallium are all made from solutions of their trichlorides. So far as we know, extractions of gold are not often made. On the other hand, the treatment is of great service in preliminary separations of the other two, for example, gallium from indium, or thallium from elements such as lead, bismuth, and cadmium. Rhenium, unlike molybdenum, remains in the acid extract under the conditions that usually obtain in an ether extraction, but like molybdenum it is quantitatively extracted by ether if a dilute hydrochloric acid solution of a perrhenate is first treated with sodium or potassium thiocyanate and stannous chloride. The solubilities of the other chlorides are chiefly of interest in so far as they may interfere in the separations that have been mentioned.

The elements do not, of course, show the same behavior in their different valences. Thus, no iron is extracted if it is bivalent, and no thallium if it is univalent. Antimony is extracted more completely if it is quinquevalent; arsenic is just the opposite, being more completely extracted when in the trivalent state. The extractions of iridium, germanium, tin, and tellurium are based on quadrivalent compounds, and of phosphorus[1] on the quinquevalent compound.

It has been claimed that small amounts (ranging from "traces" to 0.2 per cent) of copper, mercury, platinum, selenium, indium, vanadium, and zinc may remain in the ether extract. Whether these represent true solubility in the ether, or mechanical suspension resulting from faulty extraction, is not certain. At any rate, it is evident that any given separation should be carefully checked in accurate work.

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[1] For further details of the method, see Applied Inorganic Analysis by W. F. Hillebrand and G. E. F. Lundell, or Chemical Analysis of Iron and Steel by G. E. F. Lundell, J. I. Hoffman, and H. A. Bright.

PART III. METHODS FOR DETERMINING THE ELEMENTS

I. GENERAL

The commonly used methods of determining the elements are shown in Table 61. It will be noted that numerous procedures are possible, and that a given element may be determined by different methods. If several methods are available, the choice usually rests on considerations such as the amount of the element that is present, the accompanying elements, and the accuracy desired. For aluminum, which can be determined by weighing as the oxide, phosphate, or quinolate, by titrating with alkali or bromate, or by comparing colors (aurin lakes), the analyst might choose the first in tests of pure compounds of aluminum, the second in determinations where phosphorus is already present as in steels, the third in analyses of feldspar in which interfering elements such as titanium or iron are absent, or present in very small amount, the fourth in routine tests of aluminum sulphate, the fifth in routine analyses of feldspar, and the sixth in determinations of very small amounts of aluminum (< 0.1 mg) in metals and alloys. More detailed descriptions of some of the methods are given in the chapters that follow.

TABLE 61

KEY

1. Gravimetric by weighing as oxide.
2. Gravimetric by weighing as (a) chloride, (b) chloroplatinate, (c) chromate, (d) dimethylglyoxime, (e) iodide, (f) lead salt, (g) magnesium salt, (h) perchlorate, (i) pyrophosphate, (j) silver salt, (k) sulphate, (l) sulphide, (m) thiocyanate, (n) triple acetate, (o) quinolate.
3. Gravimetric by weighing as the element after (a) wet reduction, (b) fire reduction, (c) electrolysis.
4. Volumetric by titrating a specially prepared solution with (a) oxidant, (b) reductant, (c) iodometric solution, (d) neutralizing agent,* (e) precipitant, (f) cyanide solution.
5. Colorimetric (usually confined to small or moderate amounts of element).
6. Gasometric.

* Under 4 (d) are included such methods as the neutralization of $Al_2(SO_4)_3$, H_2SiF_6, or $HReO_4$ with NaOH, or $MgNH_4PO_4$ with H_2SO_4.

TABLE 61

Methods Most Commonly Used in Determining the Elements

Aluminum	1, 2i (PO_4^{---}), or o, 4c or d, 5
Antimony	1, 2l, 4a or c
Argon	6
Arsenic	2g, j or l, 4c, 5
Barium	2c or k, 4c
Beryllium	1, 5
Bismuth	1, 2a, i (PO_4^{---}) or l, 3b, 5
Boron	1 (as fixed B_2O_3), 4d
Bromine	2j, 4c or e
Cadmium	2i or k, 3c
Calcium	1, 2k, 4a
Carbon	1 (as fixed CO_2), 6 (as free CO_2)
Cerium	1, 4b or c
Cesium	2a, b, h or k
Chlorine	2j, 4c or e
Chromium	1, 4b or c, 5
Cobalt	1, 2k, 3b or c, 4b or f
Columbium	1, 4a
Copper	1, 2l or m, 3c, 4c or f, 5
Dysprosium	1
Erbium	1
Europium	1
Fluorine	2f (also as CaF_2), 4d, 5, 6
Gadolinium	1
Gallium	1
Germanium	1, 2g
Gold	3a, b or c
Hafnium	1, 2i (PO_3^-)
Helium	6
Holmium	1
Hydrogen	1 (as H_2O), 6
Indium	1
Iodine	2j, 4c or e
Iridium	3b
Iron	1, 4a, b or c, 5
Krypton	6
Lanthanum	1
Lead	2k, 3c (as PbO_2), 4c or e, 5
Lithium	2k
Lutecium	1
Magnesium	1, 2i, k or o, 4c or d
Manganese	1, 2i, k or l, 4a or b, 5
Mercury	2a, or l, 3b or c, 4e
Molybdenum	1, 2f or l, 4a or e, 5
Neodymium	1
Neon	6
Nickel	1, 2d, i or k, 3b or c, 4f
Nitrogen	4d (as NH_3), 5, 6
Osmium	3b
Oxygen	1 (as H_2O), 6
Palladium	2d, 3b
Phosphorus	2g, 4d [$(NH_4)_3PO_4 \cdot 12MoO_3 + NaOH$)], 5
Platinum	3a, b or c
Potassium	2a, b, h or k
Praseodymium	1
Radium	Electroscopic
Radon	6
Rhenium	1, 2j, 3b or c, 4a or d, 5
Rhodium	3b
Rubidium	2a, b, h or k
Ruthenium	3b
Samarium	1
Scandium	1
Selenium	3a, 4a or c
Silicon	1, 5
Silver	2a, 3b or c, 4e or f
Sodium	2a, k or n
Strontium	1, 2k
Sulphur	2k (as $BaSO_4$), 4c or e
Tantalum	1
Tellurium	3a, 4a or c
Terbium	1
Thallium	1, 2b, c, e or k, 4a or c
Thorium	1
Thulium	1
Tin	1, 4c
Titanium	1, 4a, 5
Tungsten	1, 4a or d
Uranium	1, 4a, 5
Vanadium	1, 4a or b, 5
Xenon	6
Yttrium	1
Zinc	1, 2i, k or l, 4e
Zirconium	1, 2i (PO_3^-)
Ytterbium	1

II. *GRAVIMETRIC METHODS BASED ON THE USE OF INORGANIC REAGENTS*

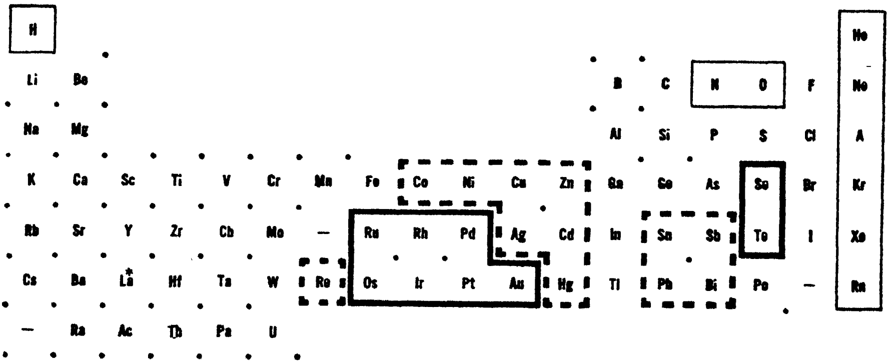
CHAPTER XXII

DETERMINATION BY WEIGHING AS THE ELEMENT

The elements that are weighed as such in chemical analyses are shown in Table 62. Of the elements regularly determined by igniting and weighing them as such, selenium, tellurium, gold, and platinum can be obtained by reduction in solutions of their compounds, followed by filtration, washing, and final ignition in the air. Gold and platinum can be ignited at red heat, but selenium and tellurium cannot be heated at temperatures above 130 and 105°C, respectively. Palladium, ruthenium, rhodium, osmium, and iridium (occasionally platinum also) are first separated as compounds, which are then decomposed by heating and finally ignited under hydrogen, or carbon dioxide in the case of palladium. Some of these elements, gold for example, can also be weighed as such after fire assay or electrodeposition.

TABLE 62

Elements Weighed as Such


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks inclose elements regularly determined by igniting and weighing as such.
Heavy broken blocks inclose elements sometimes determined by weighing as such.
Light solid blocks inclose gases that can be weighed as such.

Of the elements that are sometimes determined by weighing as such, silver and occasionally tin and lead are weighed after fire assay, bismuth after reduction in solutions of its salts or ignition of the oxide with potassium cyanide, mercury after distillation from its ores or compounds followed by amalgamation on gold or condensation in water; silver, copper, cadmium, mercury, cobalt, nickel, and, less satisfactorily, tin, antimony, bismuth, rhenium, and zinc after electrodeposition; and rhenium, cobalt, and nickel in certain cases after ignition of their oxides under hydrogen.

Ordinarily hydrogen, nitrogen, oxygen, and the noble gases are determined by measuring their volume instead of their mass if they have been separated from the other elements and from each other.

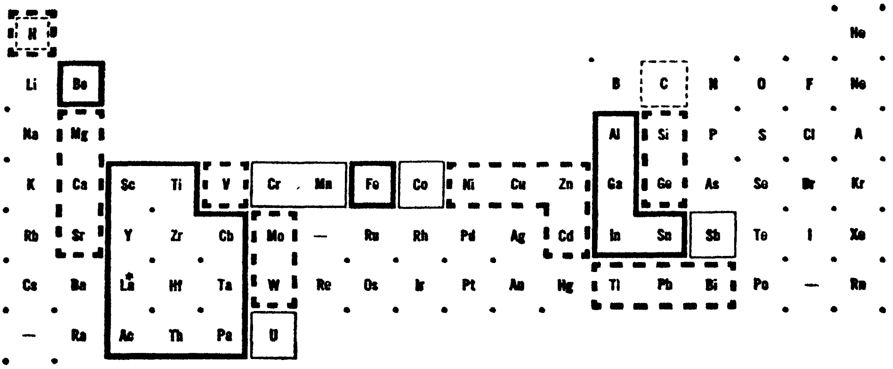
CHAPTER XXIII

DETERMINATION BY WEIGHING AS THE OXIDE

As shown in Table 63, more than half of the elements can be determined by weighing as oxides after suitable treatments. These include such diverse procedures as ignition of hydroxides (2 $Fe[OH]_3$ to Fe_2O_3), sulphides (ZnS to ZnO), carbonates ($CaCO_3$ to CaO), organic compounds (2 $Fe[C_6H_5N_2O_2]_3$ to Fe_2O_3), and earth acids ($Cb_2O_5 \cdot x\, H_2O$ to Cb_2O_5). Usually the oxides suitable for weighing are of definite composition, and consequently the methods can serve for the determination of large as well as small amounts of the elements. In general, care must be taken in ignitions of the oxides of elements 59–71, to avoid the formation of higher oxides, as with praseodymium, or the retention of acidic constituents as in ignitions of terbium sulphate or oxalate. A few oxides are not of definite composition, but approximate definite composition closely enough so that they can be used in determinations of small amounts of the elements, or in rough approximations of large amounts.

TABLE 63

Elements Weighed as Oxides


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71 (see text).

Heavy solid blocks inclose elements that can be quantitatively precipitated by NH_4OH, and ignited to oxides of definite composition.

Heavy broken blocks inclose elements that can be converted to oxides of definite composition after separation by other procedures.

Light solid blocks inclose elements that can be converted to oxides of abnormal, but reasonably definite, composition after separation by suitable procedures.

Light broken blocks inclose elements that can be converted to volatile oxides which can be absorbed in a reagent weighed before and after the absorption.

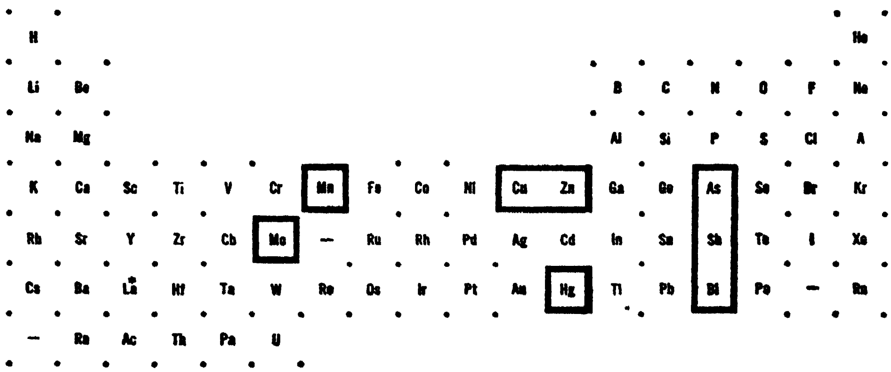
The temperatures at which oxides can be heated without volatilization or decomposition range widely; extreme care must be taken with water, whereas 1300°C or higher is permissible with silica. Usually an oxidizing atmosphere must be maintained. Special precautions must be taken if the preliminary treatments have yielded (1) compounds, like nickel dimethylglyoxime, that tend to volatilize; (2) compounds, like stannic sulphate, that are completely decomposed with difficulty; or (3) oxides, like those of magnesium, zinc, or certain rare earths, that are prone to retain absorbed gases.

DETERMINATION BY WEIGHING AS THE SULPHIDE

Although a comparatively large number of elements can be precipitated as sulphides, very few of the precipitates can be dried or ignited to yield sulphides of definite composition. Of the elements shown in Table 64, As_2S_3, MoS_3, HgS, and Bi_2S_3 can be weighed as such after drying at temperatures no higher than 110°C. Antimony can be weighed as the sulphide, Sb_2S_3, after precipitating it as either the tri- or quinquevalent sulphide and then drying at 280–300°C in an inert atmosphere such as carbon dioxide. The others must be ignited under a layer of sulphur in a crucible which is kept filled with hydrogen. When so treated, ZnS and MnS remain unchanged, while CuS is reduced to Cu_2S. Molybdenum sulphide can also be treated in this fashion, in which case it yields MoS_2.

TABLE 64

Elements That Form Sulphides Which Can Be Dried or Ignited to Yield Sulphides of Definite Composition



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

* Also elements 58–71.

Heavy blocks inclose elements that form sulphides which can be dried or ignited to yield sulphides of definite composition.

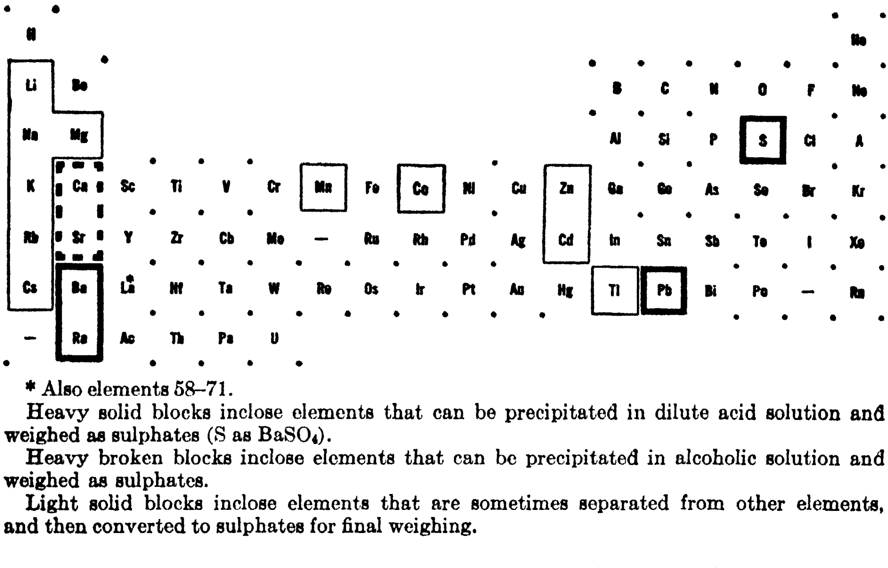
So many better methods of determining these elements are available that arsenic is the only one that is now determined to any extent by weighing as the sulphide, and then only when it is present in small amount.

DETERMINATION BY WEIGHING AS THE SULPHATE

The elements that are weighed as sulphates are shown in Table 65. Of these, barium, strontium, lead, cadmium, and sulphur (as $BaSO_4$) are often determined by weighing as sulphates. As a matter of fact, radium is determined electroscopically rather than by weighing as the sulphate, but it is worthy of note that radium sulphate is less soluble in dilute acid than barium sulphate. Calcium, magnesium, and the alkalies are occasionally weighed as the sulphates, even when present in appreciable amount. Usually, manganese, cobalt, zinc, and thallium are determined by weighing in the form of sulphates only when they occur in small amount.

TABLE 65

Elements Weighed as Sulphates


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that can be precipitated in dilute acid solution and weighed as sulphates (S as $BaSO_4$).

Heavy broken blocks inclose elements that can be precipitated in alcoholic solution and weighed as sulphates.

Light solid blocks inclose elements that are sometimes separated from other elements, and then converted to sulphates for final weighing.

The temperatures at which the sulphates can be ignited without volatilization or decomposition are approximately 500°C for manganese, cobalt, zinc, cadmium, lead, and univalent thallium; 600°C for lithium; 700°C for magnesium, sodium, potassium, rubidium, and cesium; 1000°C for calcium and strontium; and 1300°C for barium. All must be ignited in an oxidizing atmosphere, and all, save the alkaline earths, are prone to form acid sulphates that are difficult to decompose. For this reason it is necessary to treat the weighed residue with water, evaporate, ignite, and reweigh until constant weight is obtained. With rubidium and cesium this can be hastened by adding a few drops of ammonium hydroxide.

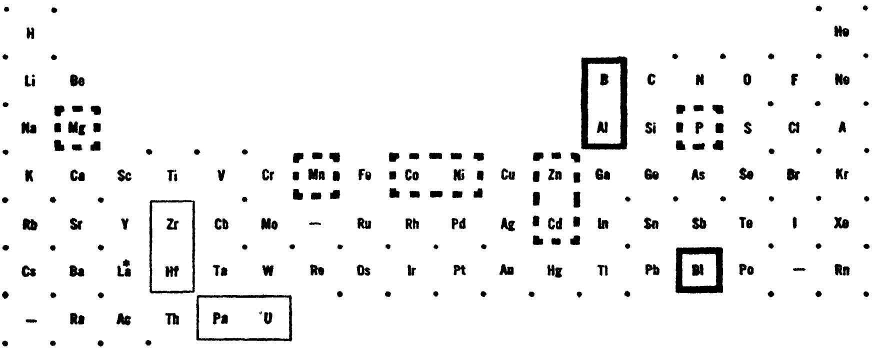
CHAPTER XXVI

DETERMINATION BY WEIGHING AS THE PHOSPHATE

The elements that can be determined by weighing as phosphate are shown in Table 66. It should be noted that only bivalent or trivalent cations react with the phosphate anion to form phosphates that are useful in gravimetric determinations. For zirconium, hafnium, and uranium the cations are ZrO^{++}, HfO^{++}, and UO_2^{++}, respectively.

TABLE 66

Elements That Can Be Determined by Weighing as Phosphates


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that are weighed as normal orthophosphates ($AlPO_4$, $BiPO_4$, BPO_4).

Heavy broken blocks inclose elements that may be weighed either as normal double orthophosphates or as pyrophosphates.

Light single blocks inclose elements that are weighed as pyrophosphate (U) or metaphosphates (Zr, Hf, Pa?).

With the exception of zirconium and hafnium (also probably protoactinium), precipitations are made in alkaline or only feebly acid solutions. As a rule, determinations must therefore be preceded by more or less laborious separations, for a large number of other elements react with the phosphate or pyrophosphate ion to yield precipitates in alkaline or only moderately acid solutions (see page 68). Most of these phosphates are either of indefinite composition (like those of Ca, Pb, Cr, and Fe) and not well suited for gravimetric determinations, or else their use (as with Li, Be, and Ag) offers no advantages over other methods. Very small amounts of calcium are sometimes gathered with magnesium and counted as the normal phosphate, $Ca_3(PO_4)_2$, although more or less of it is usually present as $Ca_2P_2O_7$

after ignition. In the case of boron the phosphate is obtained by adding an excess of diammonium phosphate to a solution of boric acid, evaporating to dryness, and finally igniting at 900°C. Phosphorus is determined by converting it to orthophosphoric acid, treating with magnesium chloride and ammonium hydroxide, filtering, washing, and finally igniting to the pyrophosphate, $Mg_2P_2O_7$.

The temperatures at which phosphates are ignited range from the 100°C required by normal double orthophosphates such as $MgNH_4PO_4 \cdot H_2O$, to the 1200°C required by the metaphosphates of zirconium or hafnium. The ignition temperatures required for the others are: 800–900°C for the pyrophosphates of Zn, Cd, Co, Ni, and U; 900°C for the normal orthophosphate of B; 1000°C for the normal orthophosphates of Al and Bi and the pyrophosphate of Mn; and 1100°C for the pyrophosphate of Mg.

CHAPTER XXVII

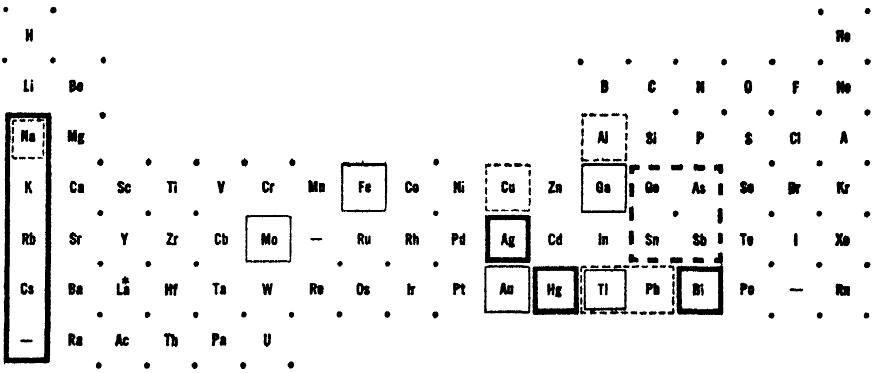
DETERMINATIONS BASED ON PROPERTIES OF THE CHLORIDES

The elements that form chlorides of special interest to analysts are shown in Table 67.

Of the chlorides that are weighed, those of silver, mercury (univalent), and bismuth (oxychloride) are precipitated, whereas those of the alkalies are obtained by evaporation after their chlorides have been separated from the other elements. Of the chlorides that can be quantitatively distilled, those of germanium and arsenic (trivalent) can be distilled at temperatures no higher than 100°C, whereas antimony (trivalent) and tin (quadrivalent) require special treatment and higher temperatures. For chlorides that may be partially volatilized see Table 14, page 29. The ether-soluble chlorides are those of the elements in their trivalent state excepting molybdenum which is sexivalent. Extraction with ether (see also Table 60, page 96) is often used to gather iron and molybdenum, quite often for gallium and

TABLE 67

Elements That Form Chlorides of Special Interest to Analysts


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that can be weighed as chlorides after precipitation or conversion.

Heavy broken blocks inclose elements that form chlorides which can be quantitatively distilled from solution.

Single solid blocks inclose elements that form chlorides which are quite soluble (over 90 per cent) in ether.

Single broken blocks inclose elements that form chlorides which are quite insoluble under certain conditions.

thallium (trivalent), and rarely for gold (trivalent). The chlorides of copper (univalent), lead, and thallium (univalent) are much less soluble than those of sodium or aluminum. Sodium chloride can, however, be precipitated and separated in large part from the chlorides of the other alkalies by saturating a cold solution with hydrochloric acid, while aluminum chloride (hydrated) can be precipitated and separated from the soluble chlorides by treating with ether and saturating with hydrochloric acid.

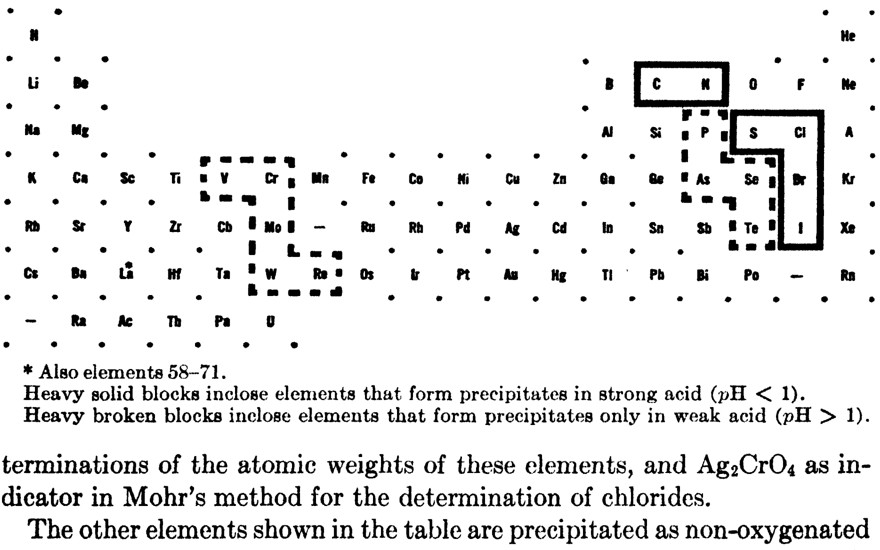
CHAPTER XXVIII

DETERMINATIONS BASED ON REACTIONS WITH SILVER

The elements that react with the silver ion to form more or less insoluble precipitates are shown in Table 68. Most of these elements react when they are present in anions of their oxygenated acids (H_3VO_4, H_2CrO_4, H_2MoO_4, H_2WO_4, $HReO_4$, H_3PO_4, H_3AsO_4, H_2SeO_3, and H_2TeO_3). Such precipitations are made in neutral or buffered acid solutions, for otherwise the resulting salts are appreciably soluble. Comparatively few of the precipitates are really useful in chemical analysis, the chief ones being Ag_3AsO_4 in determinations of small amounts of arsenic, Ag_3PO_4 and $AgReO_4$ in determinations of the atomic weights of these elements, and Ag_2CrO_4 as indicator in Mohr's method for the determination of chlorides.

TABLE 68

Elements That React with Silver to Form More or Less Insoluble Precipitates


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy solid blocks inclose elements that form precipitates in strong acid ($pH < 1$).
Heavy broken blocks inclose elements that form precipitates only in weak acid ($pH > 1$).

The other elements shown in the table are precipitated as non-oxygenated compounds in moderately acid solutions, and include AgCl, AgBr, AgI, Ag_2S, AgCN, and AgCNS. In contrast with the oxygenated compounds these are extensively used in analysis.

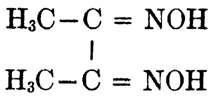
Many of the elements listed in the table also react with lead and univalent mercury or thallium to form more or less insoluble precipitates which find occasional use in analysis.

III. GRAVIMETRIC METHODS BASED ON THE USE OF ORGANIC REAGENTS

CHAPTER XXIX

PRECIPITATION BY DIMETHYLGLYOXIME

In precipitations with dimethylglyoxime



$$\begin{array}{c} H_3C-C=NOH \\ | \\ H_3C-C=NOH \end{array}$$

one of the two hydroxyl hydrogens is replaced by an equivalent of the element that is precipitated. The chief applications of the reagent are in determinations of nickel and palladium, in which the elements are precipitated as $Ni(C_4H_7N_2O_2)_2$ and $Pd(C_4H_7N_2O_2)_2$, respectively. Precipitations of nickel are usually made in ammoniacal solutions, although buffered solutions, such as one containing ammonium acetate and acetic acid, can be used. Citric or tartaric acid must always be added to prevent hydrolysis if elements such as iron or aluminum are present. Precipitations of palladium are made in cool solutions containing from 2 to 5 per cent (by volume) of hydrochloric acid. The precipitates can be dried and weighed as such, or the determination of nickel can be finished by weighing as the oxide after careful ignition, or of palladium by weighing as the metal after careful ignition and cooling in an atmosphere of carbon dioxide.

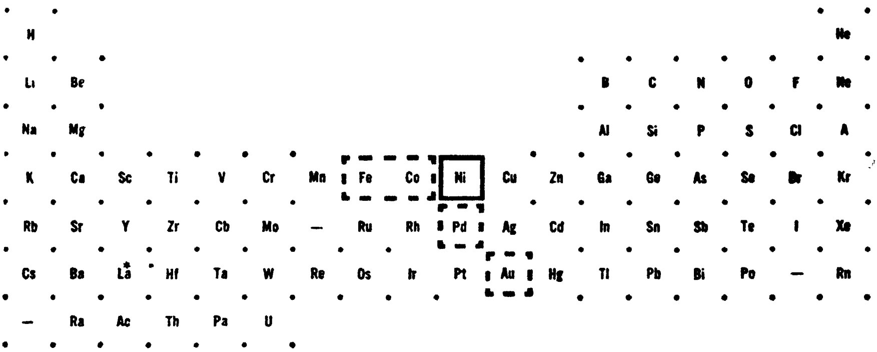
As can be seen in Table 69, very few elements cause trouble. In determinations of nickel, difficulties are caused by bivalent iron, large amounts of cobalt, palladium, and gold. Interference by the first two can easily be avoided by oxidizing them to the trivalent state before the reagent is added. Gold and palladium, on the other hand, must be removed, for palladium forms a compound with the reagent and is partially precipitated, and gold is reduced and partially precipitated as the metal.

The elements that cause difficulties in the determination of palladium are gold and selenium, which are reduced and precipitated in the metallic state. If large amounts of platinum are present, double precipitations must be made. It is understood, of course, that precipitations of palladium are not attempted in solutions that contain (1) hydrochloric acid together with elements, such as silver or univalent thallium, that form insoluble chlorides; (2) elements, such as antimony or bismuth, that hydrolyze in weak acid solutions; (3) elements, such as tungsten or columbium, that tend to deposit on standing; or (4) phosphoric acid together with elements, such as titanium or zirconium, that separate as insoluble phosphates.

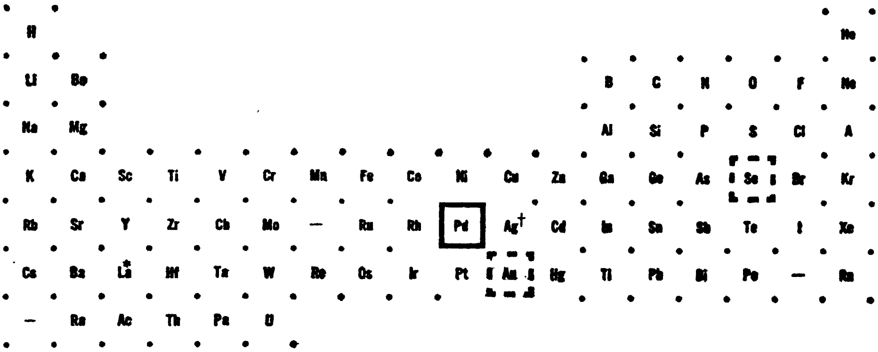
TABLE 69

Precipitation by Dimethylglyoxime

A. In solutions containing ammonium hydroxide and ammonium tartrate


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

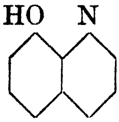
B. In *clear* diluted hydrochloric acid (3 + 97) solutions


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag† Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
† See text for behavior of silver and certain other elements.
Heavy blocks inclose elements that are quantitatively precipitated.
Broken blocks inclose elements that may be partially precipitated.

CHAPTER XXX

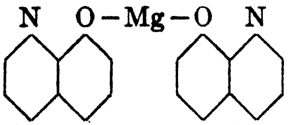
PRECIPITATION BY 8-HYDROXYQUINOLINE

8-hydroxyquinoline, , reacts with a number of elements in alkaline or buffered acid (for example, acetic acid-acetate) solutions to yield insoluble compounds in which the hydrogen of the hydroxyl group has been replaced by an equivalent of the element in question, or by a basic group such as TiO^{++}. Precipitates are not formed in solutions containing appreciable amounts ($pH < 1$) of mineral acid.

The precipitation of aluminum serves as an example of the process in a buffered acid solution and is used for the separation of aluminum from beryllium. In this precipitation, most of the free acid is neutralized with ammonium hydroxide (to a pH approximating 3.8), the solution is warmed to 60–70°C, and then there are added in succession an acetic acid solution of 8-hydroxyquinoline and 25 ml of a 2 N solution of ammonium acetate, $NH_4C_2H_3O_2$, per 100 ml of solution. The addition of the ammonium acetate brings the pH of the solution to about 5.7. After warming for about 5 minutes at 60–70°C, the precipitate is allowed to settle for 30 minutes and is filtered and washed.

The precipitation in ammoniacal solution is made as described for the buffered acid solution, except that an excess of 2–3 ml of ammonium hydroxide per 100 ml of solution is added instead of ammonium acetate.

The precipitate may be (1) ignited under a cover of oxalic acid and weighed as the oxide; (2) dried at 120°C and weighed as the anhydrous quinolate; or (3) dissolved in hydrochloric acid, treated with a standard solution of potassium bromide-bromate until it is in slight excess, and titrated with a standard solution of sodium thiosulphate after adding a solution of potassium iodide.

The steps that are followed in precipitating magnesium as the quinolate, , dissolving and brominating the precipitate, and titrating the iodine liberated by the unused bromine, can be illustrated by the equations on page 114.

$$MgCl_2 + 2\,NH_4OH + 2\,C_9H_7NO = Mg(C_9H_6NO)_2 + 2\,NH_4Cl + 2\,H_2O$$

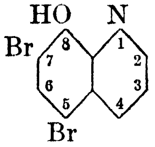
$$Mg(C_9H_6NO)_2 + 2\,HCl = 2\,C_9H_7NO + MgCl_2$$

$$3\,C_9H_7NO + 12\,HCl + 3\,KBrO_3 + 10\,KBr = 3\,C_9H_5NOBr_2 + KBr + 9\,H_2O + 12\,KCl + 3\,Br_2$$

$$3\,Br_2 + 6\,KI = 6\,KBr + 3\,I_2$$

$$3\,I_2 + 6\,Na_2S_2O_3 = 6\,NaI + 3\,Na_2S_4O_6.$$

In the above substitution, the bromine atoms enter the phenol residue in the 5–7 positions,

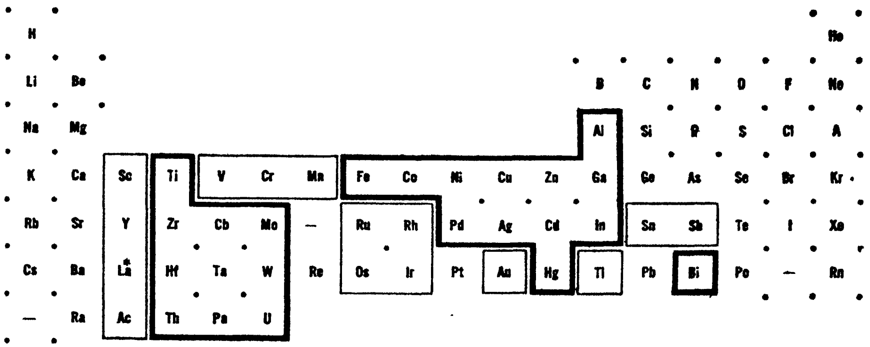


The elements that can be precipitated under the conditions that have been described are shown in Table 70. The reactions for thallium, chromium, and antimony refer to the elements in the trivalent state. Univalent thallium and quinquevalent antimony are not precipitated by 8-hydroxyquinoline under either of the conditions outlined. Cerium in the quadrivalent state is not precipitated in a buffered acid-acetate solution. In the trivalent state it is only slightly precipitated if at all. Precipitation in both valences is complete in ammoniacal solution. The behavior of the other rare earths is based on tests involving lanthanum, praseodymium, neodymium, samarium, and gadolinium. Precipitation of quadri- and quinquevalent vanadium is more nearly complete in a buffered acid-acetate solution than in an ammoniacal solution. The precipitation of trivalent antimony in a buffered acid-acetate solution and of cobalt, nickel, molybdenum, tungsten, lead, trivalent antimony, and trivalent chromium in an ammoniacal solution is nearly quantitative, whereas quadrivalent selenium and tellurium and sexivalent selenium and tellurium are not precipitated under either of the conditions set forth. Sexivalent chromium is slowly and incompletely precipitated in buffered acid-acetate solution but is not precipitated at all in ammoniacal solution. However, if precipitation is allowed to take place in the buffered acid solution and the solution is then made ammoniacal, the precipitate will not redissolve. In both types of solutions represented in Table 70, tin in either valence is incompletely precipitated, and iron in both valences is completely precipitated. Bismuth is almost completely precipitated in a buffered acid-acetate solution, not as the quinolate but probably as a basic salt. Beryllium is completely precipitated (as hydroxide and not as quinolate) in ammoniacal solution. Calcium, strontium, and barium are precipitated in part in an ammoniacal solution if they are present in large amount, or if the solution is allowed to stand for some time.

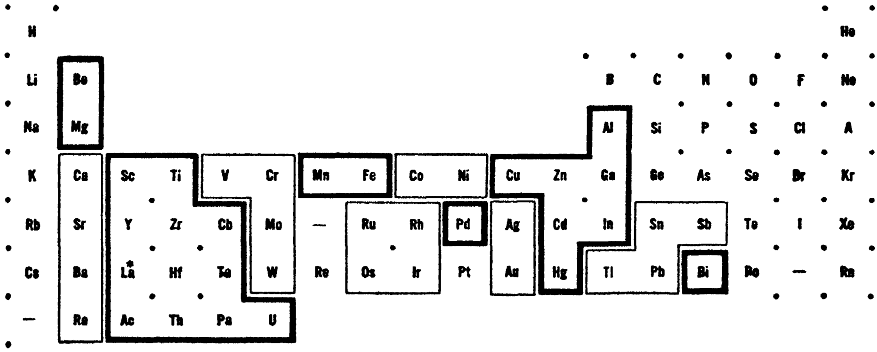
TABLE 70

Precipitation by 8-hydroxyquinoline

A: In acetic acid-acetate solution


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

B. In ammoniacal solution


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy blocks inclose elements that can be completely precipitated.

Light blocks inclose elements that may be partially precipitated.

At first glance, the number of elements that are precipitated might seem so large that the reagent would serve no useful purpose in applied analyses. There are, however, several desirable applications. For example, it can be used instead of diammonium phosphate for the precipitation of magnesium at the end of the General Procedure (page 68). This obviates the use of the phosphate reagent if determinations of the alkalies are to follow, and at the same time permits more rapid precipitation and subsequent treatment of the precipitate if magnesium must be determined. Again, it will be noted that aluminum is precipitated in an acid solution, and that beryllium is not. This difference in behavior furnishes a simple method for their separation after preliminary operations have removed other elements that would interfere.[1] Finally, some of the precipitates obtained in feebly acid solutions show wide enough differences in solubility so that the elements can be separated by carefully controlling the *p*H of the solution.

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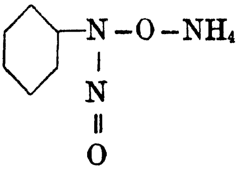
[1] For detailed descriptions of the 8-hydroxyquinoline methods, see Applied Inorganic Analysis by Hillebrand and Lundell, Chemical Analysis of Iron and Steel by Lundell, Hoffman, and Bright, or numerous articles in Z. anal. Chem. and J. Am. Chem. Soc. since 1926.

CHAPTER XXXI

PRECIPITATION BY CUPFERRON

Cupferron, the ammonium salt of nitrosophenylhydroxylamine,



reacts with a number of elements to form compounds in which the ammonium radical has been replaced by an equivalent of the element in question. Precipitations are made in cold acid solutions by treating with a filtered 6 per cent aqueous solution of the reagent until the curdy precipitate formed with the element gives way to fine white needles of the reagent. Macerated paper is then added, the solution filtered, and the precipitate washed with a cold, diluted (1 + 9) acid solution containing 1 per cent of the reagent. The precipitate decomposes at temperatures that would be required to dry it, and so it is carefully heated until gaseous compounds cease to come off, and then ignited to the oxide of the precipitated element. Reactions are usually performed in rather strong acid solutions (10 per cent by volume of sulphuric or hydrochloric acid) because otherwise so many elements would be precipitated as to render the separation useless. The elements that are precipitated or that interfere under such conditions are shown in Table 71.

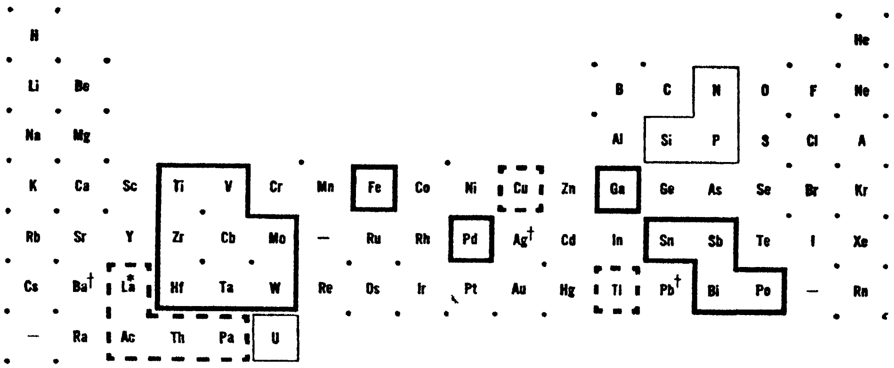
Of the interfering elements, nitrogen as nitric acid (or any other oxidizing agent) destroys cupferron, silicon is dragged down to some extent by precipitates, phosphorus forms insoluble phosphates with titanium or zirconium if much of these is present, and uranium is precipitated only if it is present in the quadrivalent state. The remaining elements react with cupferron to form more or less insoluble precipitates.

Of the elements listed as being completely precipitated, it should be remarked that precipitation of antimony is complete if it is in the trivalent state, and that no precipitation takes place at all if it is in the quinquevalent state. As for tungsten, a little of it (less than 1 mg) may remain unprecipitated. Precipitation of copper is incomplete in the strong acid solutions under discussion, but may be made complete by using less acid. Thallium is precipitated in part if in the trivalent state and not at all if in the univalent state. Barium, lead, and silver are not precipitated by cupferron, and so no precipitation takes place if an appropriate acid is used. Complete precipitation of quadrivalent vanadium requires a little more time than that of the quinquevalent compound. Complete separation of gallium from indium usually requires reprecipitation.

So far as we know, cupferron gives no precipitate in ammoniacal solutions with elements, such as copper or vanadium, that can be obtained in a clear solution, or with elements, such as iron or titanium, that can be obtained in an ammoniacal solution containing ammonium tartrate.

TABLE 71

Precipitation by Cupferron in Diluted (1 + 9) Hydrochloric or Sulphuric Acid Solution


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag† Cd In Sn Sb Te I Xe
Cs Ba† La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb† Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
† See text for behavior of barium, lead, and silver.
Heavy blocks inclose elements that can be precipitated completely or very nearly so.
Broken blocks inclose elements that may be partially precipitated.
Light blocks inclose elements that interfere under certain conditions.

As a general rule, elements such as columbium, tantalum, gallium, and the rare earths are absent, and tungsten and the members of the hydrogen sulphide group are removed before cupferron is added. The precipitation then serves for the separation of iron, vanadium, titanium, zirconium (and hafnium) from the remaining elements. Sometimes iron is also removed at the start, by adding tartaric acid to an acid solution, removing the hydrogen sulphide group, rendering the filtrate alkaline, and filtering to remove the iron sulphide. Neither tartaric acid nor hydrogen sulphide interferes in precipitations by cupferron, and so the reagent can be added to the acidified filtrate.

CHAPTER XXXII

PRECIPITATION BY α-NITROSO-β-NAPHTHOL

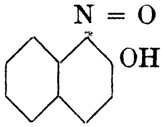
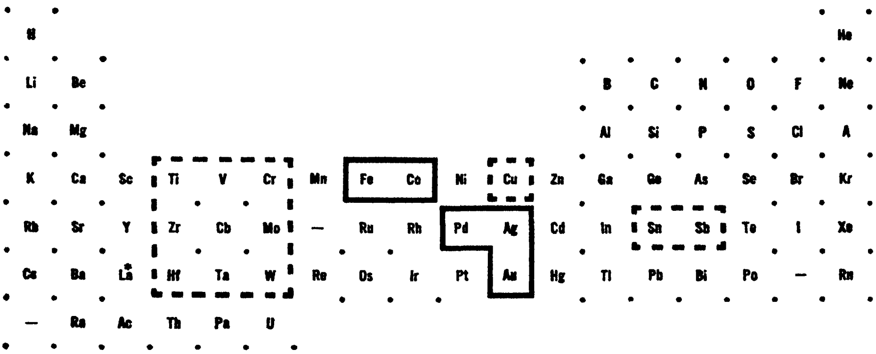
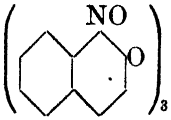
α-nitroso-β-naphthol,  OH, reacts with a number of elements to form insoluble compounds in which the hydroxyl hydrogen has been replaced by an equivalent of the element in question. Precipitations are usually made by adding the cold reagent (1 g in 15 ml of glacial acetic acid) to a diluted hydrochloric acid solution (5 + 95), heating to 60–70°C, filtering, and washing the precipitate first with hot diluted hydrochloric acid (1 + 3) and then with hot water. Elements that are precipitated under such conditions are shown in Table 72.

TABLE 72

Precipitation by α-Nitroso-β-Naphthol in Diluted (5 + 95) Hydrochloric Acid Solution


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Solid blocks inclose elements that can be completely precipitated.
Broken blocks inclose elements that may be partially precipitated.

It will be noted that the reagent is far from being selective, and that usually it will be necessary to make preliminary separations before it is possible to determine any one of the elements that can be quantitatively precipitated. As a matter of fact, the principal use of the reagent is for the determination of cobalt, after it has been separated from iron (see Precipitation by Zinc Oxide, page 90) and other interfering elements. Here the chief attraction of the method is that moderate amounts of nickel do not interfere. The precipitate has the composition,  Co, and probably contains water of hydration.

If precipitations are made in solutions containing cobalt in the divalent state, the reagent acts as both oxidant and precipitant, and its decomposition products contaminate the precipitate. The precipitate cannot, therefore, be dried and weighed as such, but must be carefully heated until gaseous products cease to come off, and then either converted to the oxide, Co_3O_4, by igniting at 750–900°C in air, or to the metal, Co, by igniting the oxide in hydrogen.[1] No contamination takes place, and the precipitate can be dried at 130°C and weighed as the hydrate $Co(C_{10}H_6ONO)_3 \cdot 2\ H_2O$ if the cobalt is oxidized to the trivalent state before the reagent is added, and precipitation is made in acetic acid solution. This method is more subject to interfering compounds than is the first and has the drawback that it is limited to the determination of small amounts of cobalt (less than 25 mg).

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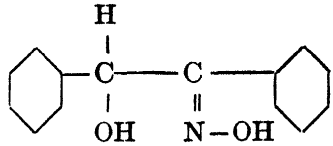
[1] For details of the method as applied in the analysis of alloy steels, see J. I. Hoffman, Bur. Standards J. Research, 7, 883 (1931); ibid., 8, 659 (1932).

CHAPTER XXXIII

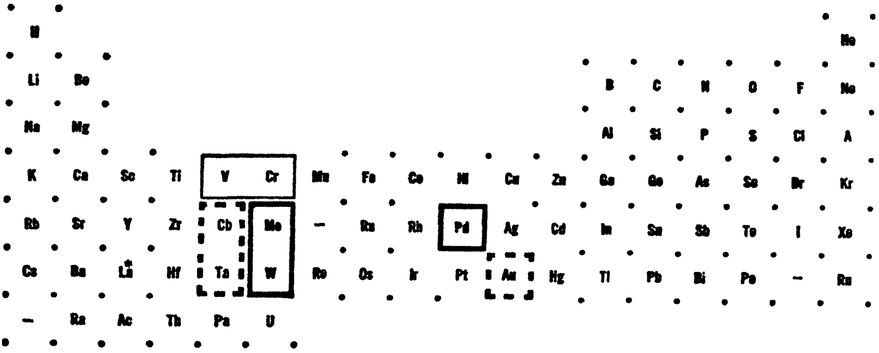
PRECIPITATION BY α-BENZOINOXIME



The principal use of α-benzoinoxime, , is for the determination of molybdenum, with which it reacts in fairly strong acid solution to form a compound, possibly $Mo(C_{14}H_{11}NO_2)_3$, in which one atom of molybdenum has replaced six hydroxyl hydrogens in three molecules of the α-benzoinoxime. The precipitation is made by adding the reagent (2 g per 100 ml of alcohol) to a cold diluted sulphuric or hydrochloric acid (5 + 95) solution of molybdenum, adding a few drops of bromine to make sure that all the molybdenum is in the sexivalent state, filtering after the addition of macerated paper, and washing the precipitate with cold diluted sulphuric acid (1 + 100) containing a little of the reagent. The precipitate cannot be weighed as such, and so is generally ignited at 500–525°C and the molybdenum weighed as the oxide, MoO_3.[1]

TABLE 73

Precipitation by α-benzoinoxime in Diluted Hydrochloric Acid (5 + 95)



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

* Also elements 58–71.
Heavy blocks inclose elements that can be completely precipitated.
Broken blocks inclose elements that may be partially precipitated.
Light blocks inclose elements that interfere under certain conditions.

Very few elements interfere, as can be seen in Table 73. Of these columbium, tantalum, gold, and palladium are seldom encountered. Tungsten is the most serious interfering element, and must be removed before precipitation is started, or else determined and deducted after the precipitate has been ignited and weighed. The precipitation of tungsten is complete if molybdenum preponderates, and is usually incomplete if tungsten occurs alone. Vanadium and chromium, which are precipitated if present in the quinquevalent and sexivalent states respectively, remain in solution and cause no trouble if they are reduced to lower valences by the addition of a little sulphurous acid before the benzoinoxime is added.

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[1] For further details of the method, see H. B. Knowles, Bur. Standards J. Research, 9, 1 (1932).

Copper is not precipitated in the presence of appreciable amounts of mineral acid. It is, however, quantitatively precipitated in ammoniacal solution, or in dilute solutions of organic acids. A method for determining it which is based on this behavior has been recommended.[2]

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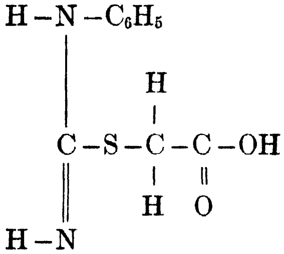
[2] F. Feigl, Ber. 56 [II], 2083 (1923).

CHAPTER XXXIV

PRECIPITATION BY PHENYLTHIOHYDANTOIC ACID

Phenylthiohydantoic acid, which has the formula



$$\begin{array}{lllll}
H-N-C_6H_5 & & & & \\
\quad | & & H & & \\
\quad | & & | & & \\
\quad C & -S- & C & -C- & OH \\
\quad \| & & | & \| & \\
\quad \| & & H & O & \\
H-N & & & &
\end{array}$$

reacts with certain elements in ammoniacal or acetic acid solution to form precipitates in which an equivalent of the element has replaced the hydroxyl hydrogen. The precipitates are not of definite composition, and cannot be weighed as such. The chief application of the reaction is for the preliminary separation of cobalt from accompanying elements, particularly in steels. In such case, the constituents of the steel are obtained in an ammoniacal solution containing ammonium citrate, and the cobalt is precipitated by heating to about 35°C, treating with a hot 3 per cent aqueous solution of the reagent as the solution is vigorously agitated, and then boiling for a few minutes. The solution is filtered at once, the precipitate washed with a 0.5 per cent solution of ammonium citrate, and the cobalt determined by a suitable method after the precipitate has been carefully ignited and fused with potassium pyrosulphate, and the melt dissolved in water.

The elements precipitated entirely or in part under such conditions are shown in Table 74. It is apparent that the method serves only as a preliminary separation, and that the cobalt in the precipitate must be determined by a method not subject to interference by the other elements that it can be expected to contain.[1] Thus, in an analysis of an alloy steel, the precipitate will contain all the cobalt and copper, a considerable part of the nickel, and a comparatively small amount of iron.

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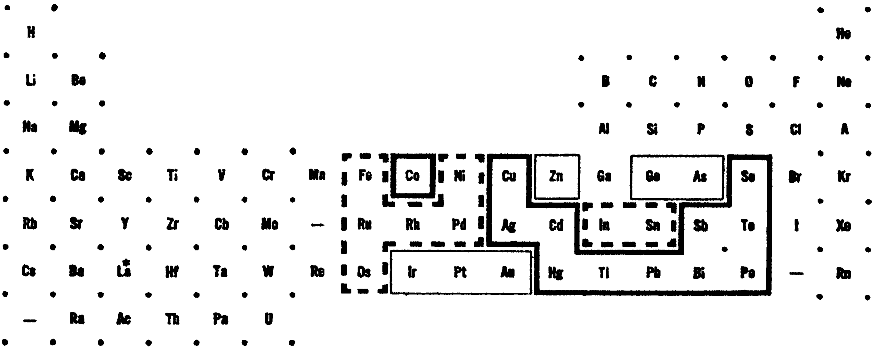
[1] For details of such methods, see H. H. Willard and Dorothy Hall, J. Am. Chem. Soc., **44**, 2219, 2226, 2237, and 2253 (1922).

TABLE 74

Precipitation by Phenylthiohydantoic Acid in an Ammoniacal Solution Containing Ammonium Citrate


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy blocks inclose elements that can be precipitated completely or nearly so.

Broken blocks inclose elements that may be partially precipitated.

Light blocks inclose elements that may interfere if present in large amount or if solutions are allowed to stand.

IV. VOLUMETRIC METHODS

CHAPTER XXXV

STANDARD SOLUTIONS AND INDICATORS USED IN VOLUMETRIC METHODS

A. Standard Solutions

It has already been stated (page 3) that "in volumetric procedures the constituent is obtained in solution, and then made to undergo a definite chemical change by the measured addition of a solution of known reacting power." The latter is called a standard solution.[1]

The standard solutions used in routine analyses are chiefly empirical. Solutions prepared on the normality basis are sometimes specified, particularly for occasional analyses, but then the term usually indicates a desirable strength rather than absolute normality.

Most empirical solutions are based on the use of a definite weight of sample, and are adjusted so that little, if any, calculation is required after the titration is finished. For the preparation of such a solution it is necessary to decide on a convenient weight of sample and a reasonable titer. The titer can represent a simple weight, such as 1 mg, or a definite percentage of the substance which is to be determined.[2] It must not be so large that errors in titration become serious, or so small that an excessive amount of the solution is required. As a rule, the solution is made a little stronger than desired, standardized, and then adjusted to the desired strength.

A normal solution is a standard solution which contains in 1 liter an amount of reagent equivalent to exactly 1.0078 g of hydrogen under the conditions which obtain when the solution is used. Such solutions are designated by the symbol *N*. Stronger or weaker solutions are expressed by integer or decimal prefixes, as, for example, 6 *N* or 0.1 *N*. Solutions that react similarly and are of exact normality are interchangeable. Thus, 1 ml of 6 *N* hydrochloric, sulphuric, perchloric, or nitric acid will neutralize exactly 1 ml of 6 *N* sodium, potassium, or barium hydroxide; 1 ml of *N* potassium dichromate or permanganate will oxidize exactly 1 ml of *N* ferrous ammonium sulphate or stannous chloride; and 1 ml of 0.1 *N* sodium arsenite or thiosulphate will react with exactly 1 ml of 0.1 *N* iodine or potassium iodate.[3]

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[1] The strength per milliliter is given the term "titer." This can be expressed in terms of the reagent in the solution or in terms of any substance with which the reagent can be made, directly or indirectly, to undergo a definite reaction. For example, the titer of a solution containing exactly 40.005 g of NaOH per liter can be given as 0.040005 g of NaOH, 0.036465 g of HCl, 0.049038 g of H_2SO_4, or 0.045008 g of $H_2C_2O_4$. Similarly, the titer of a 0.1 *N* solution of $KMnO_4$ can be expressed as 0.003161 g of $KMnO_4$, 0.0067 g of $Na_2C_2O_4$, 0.002804 g of CaO, 0.005584 g of Fe, 0.007984 g of Fe_2O_3, 0.00799 g of TiO_2, 0.01191 g of U, or 0.001698 or 0.005095 g of V, depending on whether the vanadium is oxidized from the bi- or the quadrivalent stage (V_2O_2 to V_2O_5 or V_2O_4 to V_2O_5).

[2] For example, if 5 g of steel is taken for a determination of sulphur by the evolution method, and 1 ml of the iodine solution is to represent 0.01 per cent of sulphur in the reaction $H_2S + I_2 = 2\,HI + S$, then each milliliter of iodine solution must contain $\frac{2\,I}{S} \times 0.0005$ or 0.00396 g of iodine.

Unfortunately, it is difficult to prepare exactly normal solutions. In addition, many solutions are so unstable that they would require frequent adjustment. Solutions of exact normality are, therefore, rarely prepared. Usually, the solution is made a little stronger than is theoretically required, and carefully standardized under the desired conditions. If exact normality is required, the solution is then properly diluted and restandardized. A measured solution can have the desired normality or titer only at the temperature at which it was standardized or adjusted. This restriction does not hold for weighed solutions.

Sometimes the " normality factor " of the solution is calculated. This can be based on any desired normality, and it indicates how nearly the strength of the solution approaches that normality. The normality factor is obtained either by dividing the titer that is found by the titer of a solution of the desired normality, or by dividing the volume that would have been required if the solution had been of the desired normality by the volume that was actually required.[4] The volume of a solution used in a given titration multiplied by the " normality factor " of the solution gives the volume that would have been required if the solution had the desired normality.

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[3] Before a solution of a specified normality is prepared, careful consideration must be given to the conditions under which it is to be used. For example, solutions of $KMnO_4$ are ordinarily used as oxidizing agents in acid solutions, and one-fifth of a gram-molecular weight of $KMnO_4$ (31.61 g) is required for a liter of normal solution. If, however, the oxidation is to take place in a neutral solution, one-third of a gram-molecular weight (52.68 g) must be taken. For a solution that is normal with respect to potassium, on the other hand, 1 gram-molecular weight (158.0 g) would have to be used.

[4] For example, if 30.00 ml of an approximately 0.1 *N* solution of $KMnO_4$ is required to oxidize 0.2000 g of $Na_2C_2O_4$, 1 ml is required to oxidize $\frac{0.2000}{30}$ or 0.006667 g of $Na_2C_2O_4$, and the 0.1 *N* factor is $\frac{0.006667}{0.0067}$ or 0.995. Calculated on the other basis, 0.2000 g of $Na_2C_2O_4$ requires $\frac{0.2000}{0.0067}$ or 29.85 ml of an exactly 0.1 *N* solution, and the 0.1 *N* factor of the solution must be $\frac{29.85}{30.00}$ or 0.995. The normal factor of this solution would be 0.0995.

As a matter of fact, the normality symbol is now generally used to denote the approximate rather than the actual strength of the solution. This is the meaning adopted in this book; it is useful in that it gives an instant idea of the reacting power of solutions.[5]

B. Indicators Used in Volumetric Methods

One of the prime requisites in volumetric procedures is a means of telling the exact point (the end point) at which enough of the reacting solution has been added. The more important methods of judging end points are outlined in the following sections. If the end point has been overstepped, "back titrations"[6] can be made in any one of the methods, provided (1) the method of judging the end point has not been destroyed in the course of the reaction, and (2) the reaction can be made to proceed quickly and quantitatively in the reverse direction.

Methods Used in Determining End Points

I. METHODS USED IN TITRATIONS WHICH YIELD SOLUBLE PRODUCTS

a. Neutralization Reactions

(1) *Methods based on a marked change in color at the end point.* In this very important group of volumetric methods the titration is performed in the presence of an indicator which undergoes a marked change in color within some narrow range of hydrogen-ion concentration. A list of such indicators is shown in Table 75 (page 133). It should be noted that (1) some indicators are one color (change from colorless to colored), (2) most indicators are two-colored (change from one color to a second color), and (3) a few indicators are three-colored (change from one color to a second

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[5] Among other terms used in expressing the concentration of solutions are formal, molal, molar, weight-normal, volume-molal, and weight-molal. As not all authors agree in the use of these, it is important that the reader refer to the particular author's definition of terms before attempting to make use of them. For example, one author will regard a solution containing one mole of solute per liter of solution as *molal*, whereas another calls such a solution *molar*. Again, one author defines a formal solution as one that contains a formula weight of solute in 1000 g of solvent, while another regards it as one that contains a formula weight of solute per liter of solution. There seems to be universal agreement that a weight-molal solution is one prepared by dissolving a mole of solute in 1000 g of solvent.

[6] By back titration is meant the process whereby a titration is overstepped, and the end point then found by cautiously adding small increments of a second standard solution of opposite reaction (as well as of the first solution if desired) until the reaction is considered complete. The final increments are cut down to the smallest that will produce a definite change. If the solutions are of equivalent strength, say exactly 0.1 *N*, simple subtraction indicates the volume of the first solution that was needed in the major reaction. If the solutions are not equivalent, the volumes must first, of course, be corrected to a common basis.

color at one *p*H value,[7] and then from the second color to a third color at another value). These indicators serve for the determination of hydrogen-ion concentrations ranging from *p*H 1 to *p*H 13. The indicators most often used in titrations are those that change color in the *p*H 3 to *p*H 10 range. It is obvious that in such applications it is desirable to use an indicator that undergoes a complete color change in the shortest possible range. Finally, it should be noted that small changes in hydrogen-ion concentration cause relatively large changes in *p*H near the neutral point, *p*H 7.

(2) *Methods based on a marked change in the conductivity of the solution at the end point.* Conductometric methods are based on changes of conductivity that occur when a solution of one electrolyte is added to a solution of another electrolyte. Practical applications are almost entirely restricted to solutions which contain no foreign electrolytes and which are so colored or so faintly acid or alkaline that neutralization indicators are unsatisfactory.

(3) *Methods based on a marked change in the potential of the solution at the end point.* These constitute an important and constantly growing section of volumetric analysis (see page 163).

b. Oxidation-Reduction Reactions

(1) *Methods based on changes in color at the end point.* (α) Color of one of the solutions undergoes a marked change. But few solutions answer this requirement, the chief examples being those of potassium permanganate

$$5\ H_2C_2O_4\ \text{(colorless)} + 3\ H_2SO_4 + 2\ KMnO_4\ \text{(purple)} = \\ 10\ CO_2 + K_2SO_4\ \text{(colorless)} + 2\ MnSO_4\ \text{(colorless)} + 8\ H_2O$$

and iodine

$$I_2\ \text{(yellow)} + 2\ Na_2S_2O_3\ \text{(colorless)} = \\ 2\ NaI\ \text{(colorless)} + Na_2S_4O_6\ \text{(colorless)}.$$

(β) Color of an internal indicator undergoes a marked change. These include indicators like ortho-phenanthroline ferrous complex or diphenylamine which change color at a definite oxidation potential (see Table 76, page 137), as well as indicators which form colored compounds with either of the reacting compounds. Examples of the latter type are starch in titrations of iodine, or ammonium thiocyanate in reductions of ferric ion by either stannous chloride or titanous sulphate as follows:

$$2\ Fe(CNS)_3\ \text{(red)} + Ti_2(SO_4)_3 + 3\ H_2SO_4 = \\ 2\ FeSO_4\ \text{(colorless)} + 2\ Ti(SO_4)_2 + 6\ HCNS$$

$$2\ Fe(CNS)_3\ \text{(red)} + SnCl_2 + 6\ HCl = \\ 2\ FeCl_2\ \text{(colorless)} + SnCl_4 + 6\ HCNS.$$

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[7] The symbol *p*H is a convenient way of expressing hydrogen-ion concentration; it is the negative logarithm of this value. For example, *p*H 2 represents a hydrogen-ion concentration of 10^{-2}, i.e., 0.01 g of hydrogen ion per liter of solution. The hydrogen-ion concentration of pure water is represented by *p*H 7.

(γ) Color of an external indicator undergoes a marked change. An example of these fast-disappearing methods is the use of potassium ferricyanide to show when iron has been completely oxidized from the ferrous to the ferric state by potassium dichromate:

$$6\ FeCl_2 + 14\ HCl + K_2Cr_2O_7 = 6\ FeCl_3 + 2\ KCl + 2\ CrCl_3 + 7\ H_2O$$

$3\ FeCl_2 + 2\ K_3Fe(CN)_6 = Fe_3\ [Fe(CN)_6]_2$ (Turnbull's blue) $+\ 6\ KCl$
$FeCl_3 + K_3Fe(CN)_6 =$ brown-colored compound of indefinite composition.

(2) *Methods based on a marked change in potential at the end point.* Methods of this type are fast supplanting those of the other types (see page 163).

II. METHODS USED IN TITRATIONS INVOLVING PRECIPITATES

a. A Precipitate Is Formed Continuously Until End Point Is Reached

(1) *Methods based on visual inspection.* In these methods the titrating solution is added until no more precipitate is formed in a clear solution which has been obtained by allowing the precipitate to settle, as in determinations of silver by the Gay-Lussac method

$$AgNO_3 + NaCl = AgCl + NaNO_3$$

or by filtering or centrifuging as in the precipitation of the sulphate ion by barium chloride

$$Na_2SO_4 + BaCl_2 = BaSO_4 + 2\ NaCl.$$

(2) *Methods in which an internal indicator is added.* (α) Indicator forms a soluble colored compound at the end point. An example is the use of ferric sulphate in titrations of silver nitrate or mercuric nitrate with ammonium thiocyanate.

$AgNO_3 + NH_4CNS = AgCNS$ (white precipitate) $+\ NH_4NO_3$
$Fe_2(SO_4)_3 + 6\ NH_4CNS =$
$2\ Fe(CNS)_3$ (soluble red compound) $+\ 3(NH_4)_2SO_4$.

(β) Indicator forms an insoluble colored compound at the end point. This can be illustrated by the use of the chromate ion in titrations of alkali chlorides with silver nitrate. The difference between the solubilities of silver chromate and silver chloride is so great that a permanent precipitate of the brick-red chromate cannot be obtained until all the chloride ion has been precipitated as the white chloride

$NaCl + AgNO_3 = AgCl$ (white precipitate) $+\ NaNO_3$
$Na_2CrO_4 + 2\ AgNO_3 = Ag_2CrO_4$ (brick-red precipitate) $+\ 2\ NaNO_3$.

(γ) Indicator is adsorbed by the precipitate and changes color at the end point. These are called " adsorption indicators " and consist of dyes, such as eosin or fluorescein, that change color as the result of adsorption effects on colloidal precipitates. The latter, in turn, must undergo a physical change at the end point which releases the dye and restores its original color.

(3) *Methods in which an external indicator is used.* These can be illustrated by the use of a uranyl salt to form chocolate-brown uranyl ferrocyanide as soon as enough ferrocyanide has been added to precipitate all the zinc as white potassium zinc ferrocyanide

$$3\ ZnCl_2 + 2\ K_4Fe(CN)_6 = K_2Zn_3[Fe(CN)_6]_2 \text{ (white precipitate)} + 6\ KCl$$

$$K_4Fe(CN)_6 + 2\ UO_2SO_4 = (UO_2)_2Fe(CN)_6 \text{ (chocolate-brown precipitate)} + 2\ K_2SO_4.$$

b. *Precipitate Disappears At the End Point*

An example of methods of this type is the use of a small definite amount of a precipitate of silver iodide in titrations of nickel with a solution of potassium cyanide. So long as free nickel ion is present, additions of cyanide yield the complex anion $Ni(CN)_4^{--}$

$$NiCl_2 + 4\ KCN = K_2Ni(CN)_4 + 2\ KCl.$$

When this reaction has been completed, further additions of cyanide dissolve the silver iodide to form a soluble salt

$$AgI + 2\ KCN = KAg(CN)_2 + KI.$$

c. *Precipitate Appears At the End Point*

In titrations in which the precipitate appears at the end point the reactions proceed in two stages, the first of which yields a soluble, and the second an insoluble, compound. This can be illustrated by the titration of a soluble cyanide with a standard solution of silver nitrate. The first reaction

$$2\ KCN + AgNO_3 = KAg(CN)_2 + KNO_3$$

yields the soluble compound $KAg(CN)_2$. When all the cyanide ion has been so converted, further addition of silver nitrate gives rise to the reaction

$$KAg(CN)_2 + AgNO_3 = 2\ AgCN \text{ (white precipitate)} + KNO_3$$

which yields white insoluble silver cyanide, AgCN.

d. *Precipitate Is Formed All at Once*

If the quantity of a substance to be determined is very small, the whole of it is sometimes precipitated at once and the amount estimated nephelometrically. The estimation may be made (1) visually by comparison with similarly prepared standards in suitable tubes, or (2) by the use of a photoelectric cell as an indicator. Examples are determinations involving silver chloride or barium sulphate.

e. Precipitation Causes a Marked Change in Conductivity or in Potential

In many precipitation reactions there is a sufficiently sharp change in conductivity or in potential at the end point to permit the use of conductance or potentiometric methods (see page 163).

CHAPTER XXXVI

ACIDIMETRY AND ALKALIMETRY

A. General Considerations

Acidimetry and alkalimetry cover determinations of acids and bases, and require the preparation and use of standard acid and alkaline solutions.

Hydrochloric acid is probably more frequently used as a standard acid than any other. Solutions of exact strength can be prepared by appropriate dilution of the constant-boiling acid. More often, hydrochloric acid solutions are prepared of approximate strength and then standardized either volumetrically or gravimetrically. Solutions of sulphuric acid are used occasionally, and can also be standardized volumetrically or gravimetrically. Nitric and perchloric acids are used less often and are standardized volumetrically.

By far the most commonly used standard alkaline solutions are those made from sodium hydroxide. Solutions of potassium hydroxide are more expensive and no better for ordinary purposes. Solutions of ammonium hydroxide tend to lose ammonia and are so feebly basic that their use is restricted. Solutions of barium hydroxide are sometimes used but are objectionable because they foul the apparatus unless they are protected from carbon dioxide during storage, transfer, and titration. Alkaline solutions are almost always standardized volumetrically.

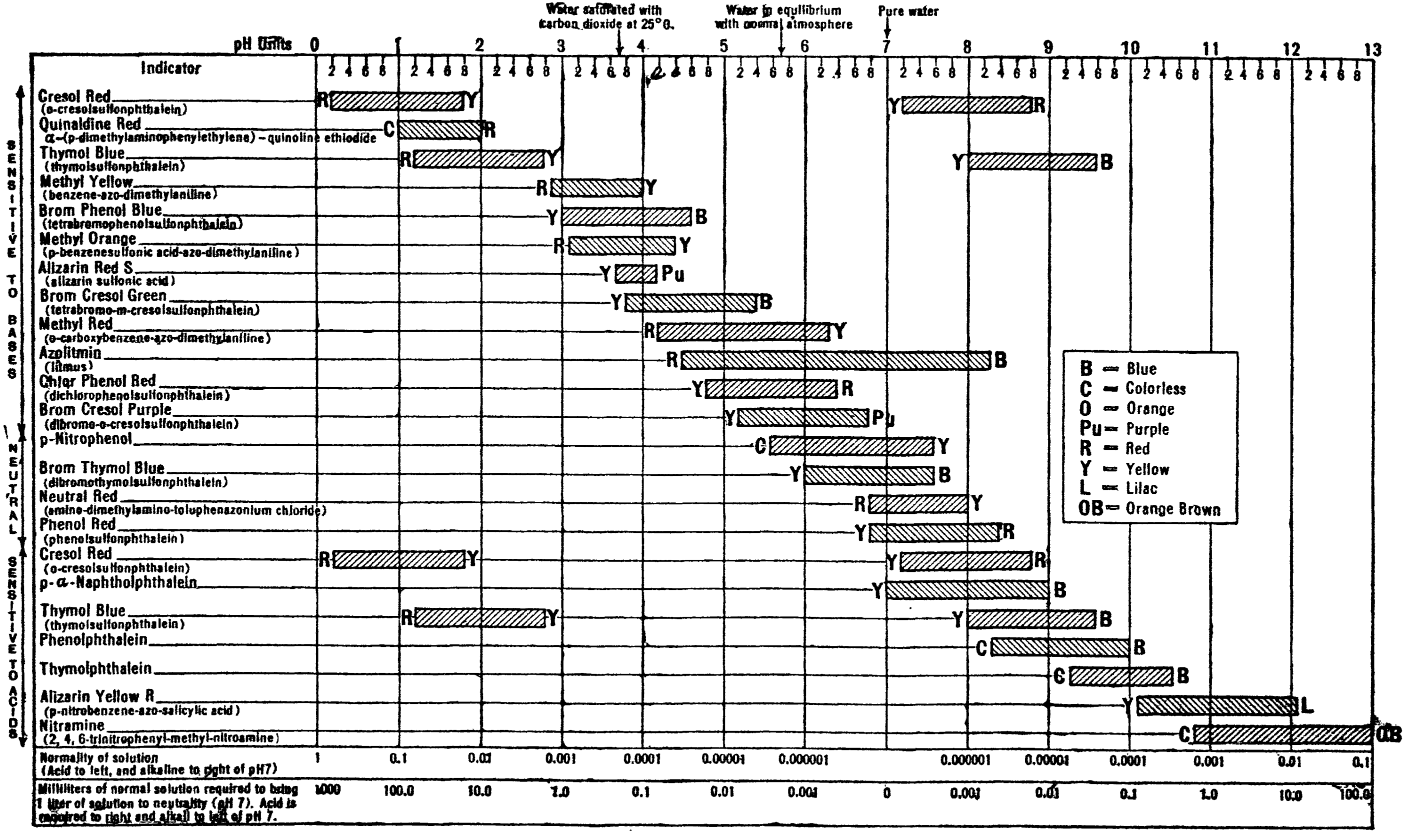
B. Indicators in Acidimetry and Alkalimetry

A list of selected indicators is shown in Table 75. These indicators may be classified as (1) *neutral,* having transition intervals at about *p*H 7; (2) *sensitive to acids,* having transition intervals at *p*H values greater than 7; and (3) *sensitive to bases,* having transition intervals at *p*H values less than 7.

With absolutely pure water the first give their transition color, the second their acid color, and the third their alkaline color. With aqueous solutions of carbon dioxide the first and second give their acid color and some of the third their alkaline color. With the last, the effect depends on the carbon dioxide content of the solution. Water saturated with carbon dioxide under a pressure of 1 atmosphere of carbon dioxide has a *p*H of about 3.7 at 25°C; water in equilibrium with the normal atmosphere containing 0.03 per cent by volume of carbon dioxide has a *p*H of about 5.7; carefully prepared conductivity water has a *p*H close to 7. Consequently the

TABLE 75

*p*H ranges of Hydrogen-ion Indicators



analyst, under the various conditions that may prevail in the laboratory, is likely to be dealing with " pure " water having a *p*H somewhere between the two extremes, *p*H 3.7 to *p*H 7. In general, therefore, the effect of carbon dioxide introduced during a titration, either from the atmosphere or from the titrating solutions, must be seriously considered if indicators that show their alkaline color at *p*H values above 4 are used. For this reason, the introduction of carbon dioxide during a titration, either from the atmosphere or from the titrating solutions, must be avoided if indicators that show their alkaline color at *p*H values above 4.5 are used.

For titrations of weak acids with strong bases, indicators sensitive to acids are required; for the titration of weak bases with strong acids, indicators sensitive to bases are needed; and for the titration of weak acids with weak bases, neutral indicators must be used, but even then titrations are often unsatisfactory. For the titration of strong acids with strong bases any of the indicators can be used, but the color transition will not indicate the same *p*H, for it will be noted that the hydrogen-ion concentrations at which neutralization indicators assume their " acid " and " alkaline " colors vary considerably, and that even with a given indicator there is a gradual transition from the one color to the other. Serious errors may therefore be introduced if a solution is standardized with an indicator that changes color at one *p*H and is subsequently used with one that changes color at another *p*H. This error is especially significant if only small volumes of the titrating solutions are used, or if the titration is made in a solution of large final volume. The magnitude of such errors can be judged by reference to the data at the bottom of Table 75.[1]

It is advisable to choose an indicator with as short a range of color change as possible, and it is necessary always to titrate to the same transition color. This is facilitated by comparison with like volumes of buffered solutions containing the same concentration of indicator, as for example solutions of *p*H 3.8, 4.0, and 4.2 to fix the pink shade of methyl orange that sets in at *p*H 4.0.

The hydrogen-ion concentration of solutions varies with dilution and with temperature, especially with weak acids or bases. Changes in temperature and in concentrations of salts in the solution may also affect certain indicators. From these and other considerations it follows that so far as possible solutions should be standardized and used (1) in the same final volume of solution, (2) at the same temperature, (3) in the same final concentration of salts, (4) with the same indicator, (5) with the same concentration of indicator, and (6) to the same transition color.

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[1] In actual tests, the amount of 0.1 *N* hydrochloric acid that was required to pass from the pink end point (about *p*H 9) of phenolphthalein to the pink end point (*p*H 4.2) of methyl orange was found to average 0.13 ml when titrations were made in 100 ml of solution, and 0.52 ml when titrations were made in 500 ml of solution.

C. Standardization of Solutions

The method of standardizing acid solutions should be chosen with regard to their history and their intended use. Hydrochloric or sulphuric acid solutions can be standardized gravimetrically by treating measured or weighed portions with silver nitrate or barium chloride, respectively, and weighing the precipitate of silver chloride or barium sulphate *provided* that (1) the solution of the acid in question is free from other acids and from compounds that yield similar anions, and (2) it is understood that the indicated acid strength will be that obtained if neutralization is carried to *p*H 7. The last also holds true of hydrochloric acid solutions prepared directly from the constant-boiling acid. The errors caused by the subsequent use of such solutions in *p*H ranges from 6 to 8 are of small moment when moderate volumes of solutions, say 100–200 ml, are involved (see Table 75). In ranges beyond these it becomes increasingly important to watch the final volumes of the titrated solution closely and to determine the magnitude of the correction that should be applied for the departure from *p*H 7.

If an acid solution is to be standardized by a volumetric method in which a color indicator is used, the analyst must decide on the *p*H to which he must titrate and then choose a suitable indicator. If the solution is that of a strong acid which is to be used in titrations involving strong acids and bases, the analyst can choose any indicator provided he is willing to make sure that carbon dioxide is excluded during titration. If he is unwilling to do this, or plans to titrate solutions of weak alkalies, he must use an indicator which is sensitive to alkalies, and gives its " alkaline " color at $p\mathrm{H} < 4.5$. If the solution is that of a weak acid, carbon dioxide *must* be excluded and indicators sensitive to acids must be used.

Acid solutions can be standardized by titration of solutions of weighed portions of chemicals such as purified sodium carbonate or borax, or by titration of standard alkaline solutions. It is preferable that the chosen indicator be used throughout standardization and subsequent use of the acid solution. If this is not feasible, and if the substitution of a second indicator is permissible, care must be taken to have the same final volume in the titrations involving the two indicators, and it is necessary to correct for the volume of standard solution required to pass from the end point chosen with the one indicator to the end point chosen with the other.

Similar considerations hold in the choosing of indicators for the standardization and use of alkaline solutions, which are almost always made from strong bases. These solutions are best standardized against acid potassium phthalate or benzoic acid if they are to be used in titrations of weak acids, and against potassium bi-iodate or standard solutions of strong acids if they are to be used in titrations of strong acids.

CHAPTER XXXVII

OXIDATION AND REDUCTION

A. General Considerations

Oxidation and reduction reactions are chemical processes in which transfers of electrons take place and corresponding changes of valence occur among atoms or groups of atoms. According to present convention, when electrons are given off, the valence of an atom or group of atoms is increased and the change is termed oxidation. When electrons are taken on, the valence is decreased and the change is termed reduction.

Oxidation and reduction always take place simultaneously, as is illustrated in the following reaction:

$$Fe^{+++} + Ti^{+++} = Fe^{++} + Ti^{++++}.$$

At the same time that Fe^{+++} gains an electron[1] and is reduced to Fe^{++}, the Ti^{+++} loses an electron and is oxidized to Ti^{++++}. The iron undergoes a decrease in valence and the titanium a corresponding increase.

It has become customary to regard substances such as permanganate, bismuthate, bichromate, and the halogens as oxidizing agents, and ferrous sulphate, sulphur dioxide, hydrogen sulphide, iodides, titanous salts, stannous chloride, and active metals in contact with non-oxidizing acids as reducing agents. There is no sharp demarcation. Hydrogen peroxide, for example, acts as a reducing agent toward permanganate and as an oxidizing agent toward iodides and many other substances. The susceptibility of a substance toward changes in valence is expressed by its oxidation or reduction potential.

B. Oxidation-Reduction Potentials

Selected oxidation-reduction potentials are shown in Table 76. In the reactions shown in the table, the oxidized form is given first; the reduced form is the first on the right of the equality sign, and the number of electrons in the equation represents the electron change occurring in the reaction as written. For example, in the equation

$$IO_3^- + 6\ H^+ + 5e = \tfrac{1}{2}\ I_2 + 3\ H_2O$$

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[1] When an ion, for example Fe^{+++}, gains an electron (a negative charge), one of its positive charges (+) is neutralized.

TABLE 76

Standard Oxidation-Reduction Potentials

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction	
*	$BiO_3^- + 6\ H^+ + 2e = Bi^{+++} + 3\ H_2O$	
*	$IO_4^- + 2\ H^+ + 2e = IO_3^- + H_2O$	
*	$1/2\ S_2O_8^{--} + e = SO_4^{--}$	
1.82	$Co^{+++} + e = Co^{++}$	
1.78	$1/2\ H_2O_2 + H^+ + e = H_2O$ (action toward reducing agents)	
1.68	$PbO_2 + 4\ H^+ + SO_4^{--} + 2e = PbSO_4 + 2\ H_2O$	
1.59	$MnO_4^- + 4\ H^+ + 3e = MnO_2 + 2\ H_2O$	
1.5	$MnO_4^- + 8\ H^+ + 5e = Mn^{++} + 4\ H_2O$	
1.49	$BrO_3^- + 6\ H^+ + 5e = 1/2\ Br_2 + 3\ H_2O$	
1.45	$Ce^{++++} + e = Ce^{+++}$	
1.45	$ClO_3^- + 6\ H^+ + 6e = Cl^- + 3\ H_2O$	
1.42	$BrO_3^- + 6\ H^+ + 6e = Br^- + 3\ H_2O$	
1.36	$Au^{+++} + 3e = Au$	
1.36	$1/2\ Cl_2 + e = Cl^-$	
1.35	$ClO_4^- + 8\ H^+ + 8e = Cl^- + 4\ H_2O$	
1.33	$MnO_2 + 4\ H^+ + 2e = Mn^{++} + 2\ H_2O$	
1.3	$1/2\ Cr_2O_7^{--} + 7\ H^+ + 3e = Cr^{+++} + 7/2\ H_2O$	
1.23	$1/2\ O_2 + 2\ H^+ + 2e = H_2O$ (in acid solution)	
1.21	$Tl^{+++} + 2e = Tl^+$	
1.20	$IO_3^- + 6\ H^+ + 5e = 1/2\ I_2 + 3\ H_2O$	
1.14	Ortho-phenanthroline-ferrous ion (J. Am. Chem. Soc., **53**, 3908 [1931]) (red in reduced, blue in oxidized form)	
1.09	$IO_3^- + 6\ H^+ + 6e = I^- + 3\ H_2O$	
1.09	$HSeO_4^- + 3\ H^+ + 2e = H_2SeO_3 + H_2O$	
1.06	$1/2\ Br_2 + e = Br^-$	
0.94	$NO_3^- + 4\ H^+ + 3e = NO + 2\ H_2O$	
0.92	$VO_3^- + H_2SO_4 + 2\ H^+ + e = VOSO_4 + 2\ H_2O$	
0.90	$Hg^{++} + e = 1/2\ Hg_2^{++}$	
0.86	$Hg^{++} + 2e = Hg$	
0.84	Diphenylamine sulphonic acid (green in reduced, reddish in oxidized form; satisfactory in presence of tungstates. J. Am. Chem. Soc., **53**, 2902 [1931])	
0.80	$1/2\ Hg_2^{++} + e = Hg$	
0.80	$Ag^+ + e = Ag$	
0.78	$Fe^{+++} + e = Fe^{++}$	
0.76	Diphenylbenzidene; green in reduced, violet in oxidized form	Unsatisfactory in presence of tungstates. See J. Am. Chem. Soc., **52**, 4179 (1930), and **53**, 2903 (1931)
0.76	Diphenylamine; colorless in reduced, violet-blue in oxidized form	
0.75	$SbO_4^{---} + 2\ H^+ + 2e = SbO_3^{---} + H_2O$	
0.74	$H_2SeO_3 + 4\ H^+ + 4e = Se + 3\ H_2O$	

TABLE 76 — *Continued*

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction
0.70	$C_6H_4O_2 + 2\,H^+ + 2e = C_6H_4O_2H_2$ (quinhydrone electrode)
0.68	$1/2\,O_2 + H^+ + e = 1/2\,H_2O_2$ (reducing action toward stronger oxidants)
0.66	$MnO_4^- + e = MnO_4^{--}$
0.59	$MnO_4^- + 2\,H_2O + 3e = MnO_2 + 4\,OH^-$
0.57	$AsO_4^{---} + 2\,H^+ + 2e = AsO_3^{---} + H_2O$
0.53	Methylene blue at pH 2.86 [Hygienic Lab. Bul. **171**, p. 191 (1928)]
0.53	$1/2\,I_2 + e = I^-$
0.5	$MoO_3 + 4\,H^+ + e = MoO^{+++} + 2\,H_2O$
0.49	$Fe(CN)_6^{---} + e = Fe(CN)_6^{----}$
0.47	$H_2SO_3 + 4\,H^+ + 4e = S + 3\,H_2O$
*0.4	$VO_3^- + 6\,H^+ + 3e = V^{++} + 3\,H_2O$
0.4	$VO^{++} + 2\,H^+ + e = V^{+++} + H_2O$
*0.4	$PtCl_6^{--} + 2e = PtCl_4^{--} + 2\,Cl^-$
0.40	$1/2\,O_2 + H_2O + 2e = 2\,OH^-$
0.36	$UO_2SO_4 + 4\,H^+ + SO_4^{--} + 2e = U(SO_4)_2 + 2\,H_2O$
0.34	$Cu^{++} + 2e = Cu$
0.333	Decinormal calomel electrode
*0.3	$WO_3 + 4\,H^+ + e = WO^{+++} + 2\,H_2O$
0.280	Normal calomel electrode
0.23	$AgCl + e = Ag + Cl^-$
0.2	$PtCl_4^{--} + 2e = Pt + 4\,Cl^-$
0.2	$Bi^{+++} + 3e = Bi$
0.17	$S + 2\,H^+ + 2e = H_2S$
0.17	$Cu^{++} + e = Cu^+$
0.15	$Sn^{++++} + 2e = Sn^{++}$
0.14	$SO_4^{--} + 4\,H^+ + 2e = H_2SO_3 + H_2O$
*0.1	$WO^{+++} + 2\,H^+ + e = W^{+++++} + H_2O$
0.04	$TiO^{++} + 2\,H^+ + e = Ti^{+++} + H_2O$
*0.0	$MoO_3 + 6\,H^+ + 3e = Mo^{+++} + 3\,H_2O$
0.000	$H^+ + e = 1/2\,H_2$
*−0.1	$1/2\,Cb_2O_5 + 5\,H^+ + 2e = Cb^{+++} + 5/2\,H_2O$
−0.12	$Pb^{++} + 2e = Pb$
−0.14	$Sn^{++} + 2e = Sn$
*−0.2	$CO_2 + H^+ + e = 1/2\,H_2C_2O_4$
−0.2	$V^{+++} + e = V^{++}$
−0.21	$SbO^+ + 2\,H^+ + 3e = Sb + H_2O$
−0.23	$Ni^{++} + 2e = Ni$
−0.29	$Co^{++} + 2e = Co$
−0.34	$Tl^+ + e = Tl$
−0.38	$In^{+++} + 3e = In$
−0.40	$Cd^{++} + 2e = Cd$
−0.40	$Cr^{+++} + e = Cr^{++}$
−0.44	$Fe^{++} + 2e = Fe$

TABLE 76 — *Continued*

Oxidizing Potential Referred to Normal Hydrogen Electrode = 0	Reaction
−0.5	$Ga^{+++} + 3e = Ga$
−0.56	$Cr^{++} + 2e = Cr$
−0.76	$Zn^{++} + 2e = Zn$
−0.83	$H_2O + e = 1/2\ H_2 + OH^-$
−1.1	$Mn^{++} + 2e = Mn$
−1.4	$U^{++++} + 4e = U$
−1.69	$Be^{++} + 2e = Be$
−1.7	$Al^{+++} + 3e = Al$
−2.40	$Mg^{++} + 2e = Mg$
−2.71	$Na^+ + e = Na$
−2.76	$Ca^{++} + 2e = Ca$
−2.90	$Ba^{++} + 2e = Ba$
−2.92	$Sr^{++} + 2e = Sr$
−2.92	$K^+ + e = K$
−2.93	$Rb^+ + e = Rb$
−2.96	$Li^+ + e = Li$

* Approximate value or position. See text.

IO_3^- represents the oxidized form, I_2 represents the reduced form, and 5 represents the electron change, which is also the valence change when iodate is reduced to elemental iodine. If the reduction is carried one stage farther, the reaction is represented by the equation

$$IO_3^- + 6\ H^+ + 6e = I^- + 3\ H_2O.$$

Here iodine in the oxidized form has a valence of 5 and in the reduced form a valence of 1, although 6 electrons are involved in the reaction. The number of electrons, rather than the apparent valence change, indicates the available oxidizing power of the reaction. This becomes clearer if it is assumed that in the latter reaction iodine passes from a valence of +5 to a valence of −1.

Departures from the usual ionic form of equation are occasionally made for the sake of clarity. Values given to only one decimal are not as certain as those given to two places. Reactions marked with an asterisk are approximately placed, the value of the potential in most of these reactions having been estimated from meager data on entropies and heats of reaction or other thermodynamic values. The table is intended primarily as a guide to the analytical chemist, and, if other potentials or more complete information is desired, it may be necessary to consult original sources or such reference works as International Critical Tables, Vol. 6, McGraw-Hill Book Co., New York, 1929, and Reference Book of Inorganic Chemistry by Latimer and Hildebrand, the Macmillan Co., New York, 1933.

A study of oxidation-reduction potentials affords a means of determining whether a given reaction can proceed, that is, whether a given system can act as an oxidizing or reducing agent toward another system. The potentials shown in Table 76 are referred to the potential of the hydrogen-hydrogen ion couple as zero, and are based on unit activity of all the substances concerned at 25°C. They represent the emf that would be set up between the electrodes of a cell consisting of the substances represented by the couple or half-cell on the one side and the hydrogen electrode on the other. Frequently, potentials cannot be measured by setting up such cells but are calculated from equilibrium data (free energy) or from entropies and heats of reaction.

These potentials indicate whether a given oxidation or reduction can proceed when properly catalyzed. They do not show whether the speed of the reaction is great enough to make the process satisfactory, or whether we know the catalyst that will make it so. It is generally true that (given the proper catalyst where necessary) substances near the top of the list, like potassium permanganate or potassium dichromate, will oxidize the reduced form of the substances that stand considerably below them. Conversely, the substances in the lower part of the list, such as stannous chloride, titanous chloride, or metallic zinc in contact with non-oxidizing acids, should reduce the oxidized form of the substances that stand well above them.

A very good example of substances for which a catalyst is needed to make a reaction experimentally realizable is furnished by ceric sulphate and arsenious acid. Ceric sulphate (potential = 1.45) does not oxidize arsenious acid (potential = 0.57) at all satisfactorily in the absence of a catalyst, whereas it easily oxidizes ferrous to ferric iron (potential = 0.78). It can be said in general for that part of the table in which the potentials are well established that, if two reactions are set down in the order given in the table, they can take place in a clockwise direction, and they will not take place in the opposite direction when the substances involved are brought together. This is shown schematically by the oxidation of ferrous iron by ceric sulphate as follows:

$$\begin{array}{lll} 1.45 & Ce^{++++} + e \rightarrow Ce^{+++} \\ 0.78 & Fe^{+++} \;\; + e \leftarrow Fe^{++} \end{array}$$

It should be remembered that factors such as catalysts, temperature, and acid concentration necessary to prevent hydrolysis, or essential to the reaction, may make considerable difference in the rate and direction of a reaction. For example, the reaction between arsenite and iodine: $AsO_3^{---} + I_2 + H_2O \rightleftarrows AsO_4^{---} + 2\,I^- + 2\,H^+$, is quantitative from left to right in neutral solution and nearly quantitative from right to left in strongly acid solution. It can be said, in general, that those reactions like the above, in which H^+ takes part, are directly influenced by changes in acid concentration, whereas those in which H^+ does not take part are usually influenced to only a minor degree.[2] The reactions between ferric and titanous ions or ceric and ferrous ions are examples of the latter:

$$Fe^{+++} + Ti^{+++} = Fe^{++} + Ti^{++++}$$
$$Ce^{++++} + Fe^{++} = Fe^{+++} + Ce^{+++}.$$

As previously stated, oxidation and reduction take place simultaneously during a titration. In titrating an oxidant with a reductant, the solution at first has the potential of the oxidant and changes only slightly as the reductant is added. When all the oxidant has been reduced, the potential of the solution drops (abruptly in reactions that are satisfactory analytically) to that of the reductant. Similarly, when ferrous iron is titrated with ceric sulphate, the ratio $\frac{Fe^{+++}}{Fe^{++}}$ is the determining factor until the last trace of iron is oxidized; then the ratio $\frac{Ce^{++++}}{Ce^{+++}}$ becomes the determining factor, and the potential of the solution quite abruptly changes from that of the ferrous-ferric system (+0.78) to that of the ceric-cerous system (+1.45). The magnitude and abruptness of this change are factors in the determination of end points by oxidation and reduction indicators or by potentiometric means.

As has already been intimated, the end points of oxidation and reduction reactions may also be determined by means of oxidation and reduction indicators which change color with change in potential. Indicators of this type are not so well understood and classified as the neutralization indicators. A few of the more useful oxidation-reduction indicators are included

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[2] The expression for the oxidation-reduction potential of the reaction

$$MnO_4^- + 8\,H^+ + 5e = Mn^{++} + 4\,H_2O$$

is

$$E = E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-]\,[H^+]^8}{[Mn^{++}]}$$

or

$$E = E_0 + \frac{0.0591}{5}\log\frac{[MnO_4^-]}{[Mn^{++}]} + \frac{0.0591}{5}\log\,[H^+]^8$$

By means of the latter form the effect of change in hydrogen-ion concentration can be estimated, or the effect of change in the ratio $\frac{[MnO_4^-]}{[Mn^{++}]}$ at constant pH can be calculated. Theoretically the quantities in brackets are to be expressed in terms of activity, but, for approximate calculations, concentrations may be used. For graphs on the effect of acidity see The Determination of Hydrogen Ions by Clark, pages 385–387, The Williams and Wilkins Co., Baltimore, Md., 1928.

in the table of electrode potentials in order to aid the analyst in choosing the one best suited for the determination at hand. To these might be added methyl orange and methyl red which are colored in reducing solutions and irreversibly lose their colors when an excess of certain oxidizing agents is added.

C. General Applications

The elements that can be determined by oxidation-reduction methods are listed in Table 77, and a few reduction-oxidation methods are discussed in detail in the sections that follow. Examples of oxidation-reduction methods are presented on pages 198 and 202.

D. Selected Applications

I. REDUCTION WITH STANNOUS CHLORIDE

A number of chemical compounds can be reduced by stannous chloride, but only a few of the reactions are useful in chemical analyses. The only one that is widely used in volumetric analyses is its reaction with iron. This is of importance because the reduction proceeds to the bivalent state and forms the basis of volumetric determinations of iron. These can be made by direct titration with a standard solution of stannous chloride, the end point being found potentiometrically or by means of an indicator such as ammonium thiocyanate. More often, reducing compounds such as carbonaceous matter or elements in their lower valences are first oxidized by adding a slight excess of permanganate, and the iron is then reduced in hydrochloric acid solution by heating to boiling and adding a *slight* excess of stannous chloride, as judged by the disappearance of the yellow color of ferric chloride. The iron is then determined by diluting the solution, adding mercuric chloride to oxidize the excess of stannous chloride, next adding titration mixture ($H_3PO_4 + MnSO_4 + H_2SO_4$) if permanganate is to be used, and finally titrating with a standard oxidizing solution. The reactions that take place in such a determination are illustrated by the following equations:

$$2\,FeCl_3 + SnCl_2 = 2\,FeCl_2 + SnCl_4$$

$$SnCl_2 + 2\,HgCl_2 \text{ (large excess)} = SnCl_4 + 2\,HgCl$$

$$6\,FeCl_2 + K_2Cr_2O_7 + 14\,HCl = 6\,FeCl_3 + 2\,KCl + 2\,CrCl_3 + 7\,H_2O$$

or

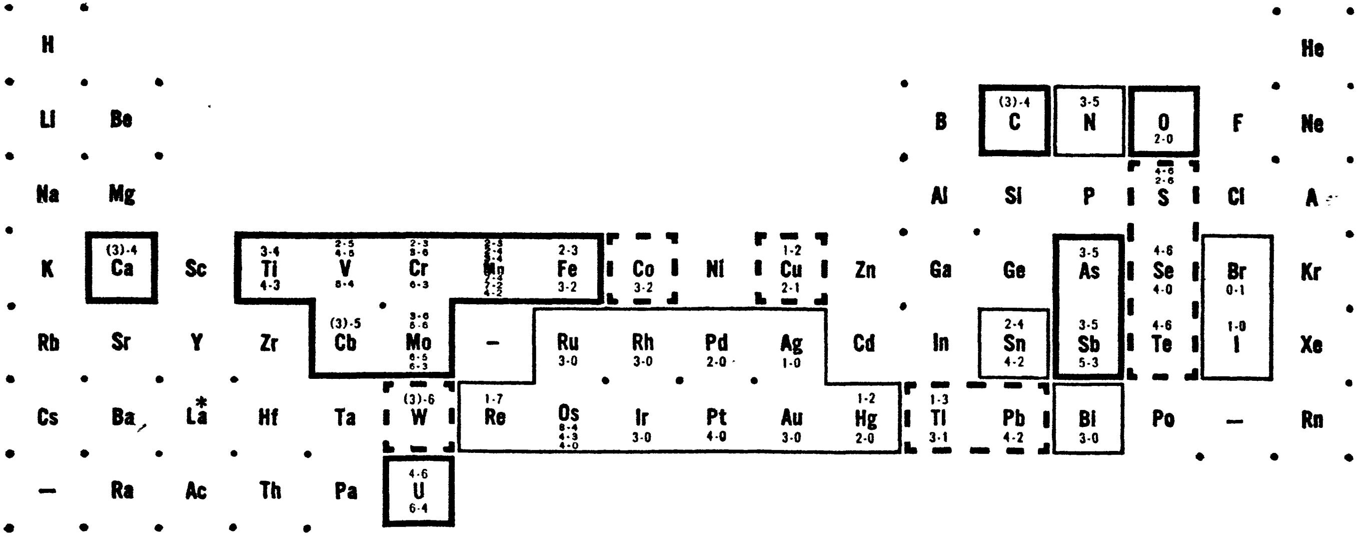
$$10\,FeCl_2 + 2\,KMnO_4 + 16\,HCl + \text{(titrating mixture)} = 10\,FeCl_3 + 2\,KCl + 2\,MnCl_2 + 8\,H_2O.$$

The other elements that are affected by such treatments (stannous chloride added in *very slight* excess, then mercuric chloride in large excess, and

TABLE 77

Volumetric Determinations Involving the Use of a Standard Oxidizing ($KMnO_4$, $K_2Cr_2O_7$, $Ce(SO_4)_2$) or Reducing ($FeSO_4$, $Ti_2(SO_4)_3$, Na_2HAsO_3, $SnCl_2$, $CrSO_4$) Solution

(Iodometric procedures are not included. For these, see page 151. Numbers above elements represent valence changes in oxidations; those below represent reductions)



* Also elements 58–71, excepting **Ce** 4·3 and 2·3 **Eu** 2·3 **Yb**

Heavy solid blocks inclose elements often determined.
Heavy broken blocks inclose elements occasionally determined.

Light solid blocks inclose elements for which methods have been proposed, but seldom used.

Titrations under carbon are those involving the breaking of a C–C bond as in oxalic acid. This covers calcium also.

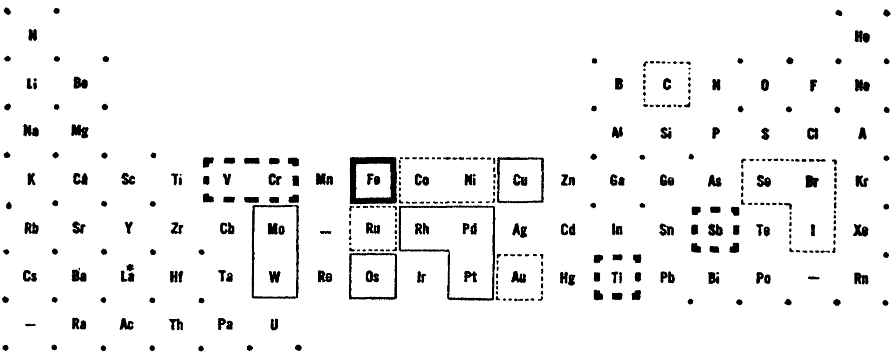
Titrations under oxygen are those involving hydrogen peroxide.

titration in cold dilute solution) are shown in Table 78. Of these, vanadium may be reduced below the quadrivalent state by the small excess of stannous chloride used, but is apparently reoxidized to the quadrivalent state during the dilution of the solution and treatment with mercuric chloride. If proper indicators are chosen, it need not interfere in the determination of iron, for no oxidation of quadrivalent vanadium can occur until the iron has been completely oxidized. With permanganate alone, this is even foreshadowed quite accurately by the first momentary pink flush that suffuses the whole solution. Mercury, as mercuric chloride, which is added to oxidize stannous chloride when it has been used in excess, is reduced to univalent mercurous chloride which is white and does not react with the oxidant; in such applications, a large excess of mercuric chloride must be added at one stroke, for otherwise the reduction yields the element which appears black in the finely divided form

TABLE 78

Reduction by Stannous Chloride in Diluted (1 + 1) Hydrochloric Acid

(With particular reference to the Zimmermann-Reinhardt method for iron)


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid block denotes reduction to a definite state and reoxidation to a definite state.

Heavy broken blocks inclose elements that are reduced to a definite state and reoxidized to an indefinite state.

Light solid blocks inclose elements that are reduced to an indefinite state and reoxidized to definite or indefinite states.

Light broken blocks inclose elements that cause difficulties as described in the text.

$$SnCl_2 + HgCl_2 = Hg + SnCl_4$$

and prevents a visual estimation of the end point.

As for the rest, (1) molybdenum, platinum, osmium, and palladium are reduced and form compounds which consume appreciable amounts of the oxidant; (2) antimony, copper, and rhodium form compounds which cause a slight consumption of the oxidant; (3) such amounts of tungsten as may survive the preliminary attack form compounds that consume permanganate and also interfere because of their color; (4) gold and ruthenium yield colored solutions and selenium a colored precipitate which conceal the end point but do not react with the oxidant; (5) the reduction products of chromium (trivalent) and thallium (univalent) react so slowly with the oxidant under the conditions that, like vanadium, their effects are usually negligible; (6) bromine and iodine must be removed at the start of the determination, for their halogen acids react with the oxidant; and (7) on account of the color of their solutions, cobalt and nickel interfere if present in large amount.

The reduced compound of molybdenum is of special importance, for it yields a colored compound with thiocyanic acid which can be extracted by ether and used for the colorimetric determination of molybdenum. If a large excess of stannous chloride is used, rhenium yields a compound that reacts similarly.

II. Reduction with Sulphur Dioxide

Of the elements reduced by sulphur dioxide in acid solution, three—iron, vanadium, and antimony—form definite compounds which can be reoxidized by titrating with a standard oxidizing solution. Determinations of iron and vanadium are usually made in diluted sulphuric acid (2.5 + 97.5) solutions by (1) adding sulphuric acid and evaporating to fumes of the acid if chlorides, bromides, iodides, nitrates, or large amounts of organic matter are present; (2) diluting and treating with permanganate in slight excess to make sure of the oxidation of organic or other reducing compounds; (3) heating to boiling; (4) treating with a current of sulphur dioxide or a freshly prepared solution of sulphurous acid; (5) boiling to expel the excess of sulphur dioxide; and (6) titrating with a standard solution of potassium permanganate. Sulphur dioxide can be expelled by boiling in the open in the case of vanadium or antimony, for their reduced compounds are stable. Bivalent iron, on the other hand, is not stable, and its solutions must be boiled under an atmosphere of carbon dioxide. The titrations also require different conditions, that of vanadium being done in hot solution, that of iron in cool solution, and that of antimony in a cold solution containing hydrochloric in addition to sulphuric acid.

In such determinations, iron is reduced to the bivalent and reoxidized to the trivalent state, antimony is reduced to the trivalent and reoxidized to the quinquevalent state, and vanadium is reduced to the quadrivalent and reoxidized to the quinquevalent state. The reactions involved can be illustrated by the following equations:

$$Fe_2(SO_4)_3 + H_2SO_4 + SO_2 + 2\,H_2O = 2\,FeSO_4 + 3\,H_2SO_4$$

$$2\,H_3VO_4 + H_2SO_4 + SO_2 = V_2O_2(SO_4)_2 + 4\,H_2O$$

$$2\,H_3SbO_4 + H_2SO_4 + 2\,SO_2 = Sb_2(SO_4)_3 + 4\,H_2O$$

$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$$

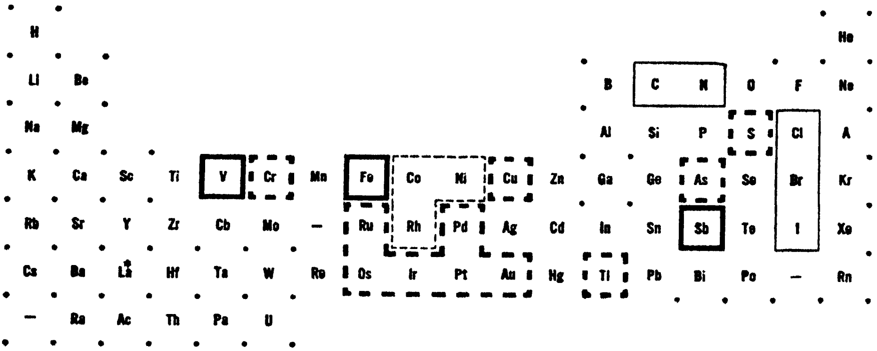
$$5\,V_2O_2(SO_4)_2 + 2\,KMnO_4 + H_2SO_4 + 22\,H_2O = 10\,H_3VO_4 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2SO_4$$

$$5\,Sb_2(SO_4)_3 + 4\,KMnO_4 + H_2SO_4 + 24\,H_2O = 10\,H_3SbO_4 + 2\,K_2SO_4 + 4\,MnSO_4 + 10\,H_2SO_4.$$

Elements that interfere in these determinations are shown in Table 79. Chief among these are arsenic, palladium, platinum, and osmium, which form compounds that consume permanganate. The same is true of thallium, chromium, and, to a very slight extent, rhodium, if titrations are made in hot solutions. The consumption of permanganate by copper, or by moderate amounts of chromium in cool solution, is so slight that it can usually be disregarded. Iridium and ruthenium no doubt consume permanganate, but they are especially objectionable because they yield colored compounds that hide the end point. Gold is reduced to the metallic state and must be removed before the titration. Sulphur, as certain thio compounds introduced through the use of old solutions of sulphurous acid, may consume appreciable amounts of permanganate.

TABLE 79

Reduction by Sulphur Dioxide in Dilute (1 + 99) Sulphuric Acid


H
He
Li Be
B C N O F Ne
Na Mg
Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.
Heavy blocks inclose elements that are reduced to definite valences.
Broken blocks inclose elements that may interfere in titrations of the reduced compounds.
Light solid blocks inclose elements that are removed at the start of the determination.
Light broken blocks inclose elements that interfere if present in large amount on account of the color of their solutions.

III. Reduction with Hydrogen Sulphide

Reduction by hydrogen sulphide, followed by titration with a standard oxidizing solution such as potassium permanganate, is not used as much today as in the past for the determination of iron and vanadium. The determination of iron is made by (1) adding sulphuric acid and evaporating to fumes of the acid if chlorides, bromides, iodides, nitrates, or large amounts of organic matter are present; (2) diluting so that the solution contains approximately 2.5 ml of sulphuric acid per 100 ml; (3) adding potassium permanganate in excess and boiling to make sure of the destruction of organic matter; (4) passing in a current of hydrogen sulphide, first at room temperature and then as the solution is heated to boiling; (5) adding enough sulphuric acid to bring the acidity to 10 per cent by volume; (6) expelling hydrogen sulphide by boiling vigorously in a stoppered flask through which a current of carbon dioxide is passed; (7) cooling to room temperature; and (8) titrating with a standard solution of potassium permanganate. In determinations of vanadium, the titration is made in hot solution and the use of carbon dioxide is not necessary, for the reduced vanadium compound needs no protection from the air. The reactions involved in such determinations can be illustrated by the following equations:

$$Fe_2(SO_4)_3 + H_2SO_4 + H_2S = 2\,FeSO_4 + 2\,H_2SO_4 + S$$

$$2\,H_3VO_4 + 2\,H_2SO_4 + H_2S = V_2O_2(SO_4)_2 + 6\,H_2O + S$$

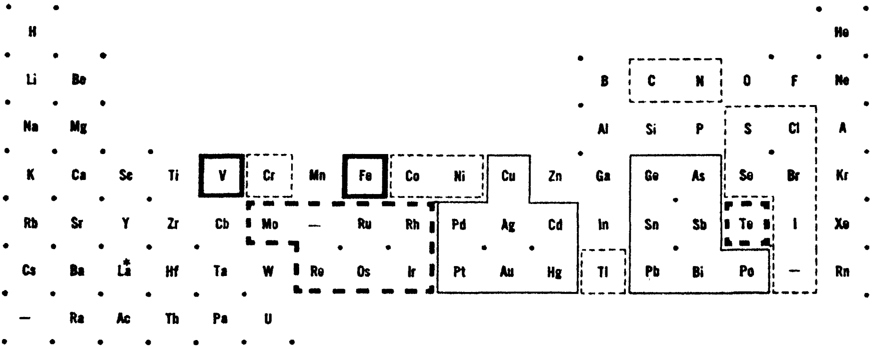
$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2O$$

$$5\,V_2O_2(SO_4)_2 + 2\,KMnO_4 + H_2SO_4 + 22\,H_2O = 10\,H_3VO_4 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2SO_4.$$

The elements affected by such treatments are shown in Table 80. Of these, reduction proceeds quantitatively to the bivalent state with iron, to the quadrivalent state with vanadium, and to the univalent state with thallium. In the titration, iron is oxidized to the trivalent, and vanadium to the quinquevalent, state. Thallium is reoxidized to the trivalent state, the reaction proceeding more rapidly in hot than in cool solutions, but never quantitatively under the conditions of the experiment. Of the remaining elements, the most troublesome are the soluble thio compounds that are formed as a result of side reactions, and which are difficult to decompose by treatments that will not affect the reduced iron or vanadium compounds. If left in solution, they react with the titrating solution and cause high results. For the most part, the members of the Hydrogen Sulphide Group cause no trouble, except that they had best be removed by filtration before expelling the hydrogen sulphide. A few members of the group may, however, remain in solution as colloidal sulphides or as partially reduced compounds which afterwards react with the titrating solution. Of these, molybdenum, tellurium, iridium, ruthenium, and osmium interfere to a moderate, and rhenium and rhodium to a slight, extent. Chromium interferes because it is oxidized by permanganate,

TABLE 80

Reduction by Hydrogen Sulphide in Diluted (2.5 + 97.5) Sulphuric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that are reduced to definite valences.

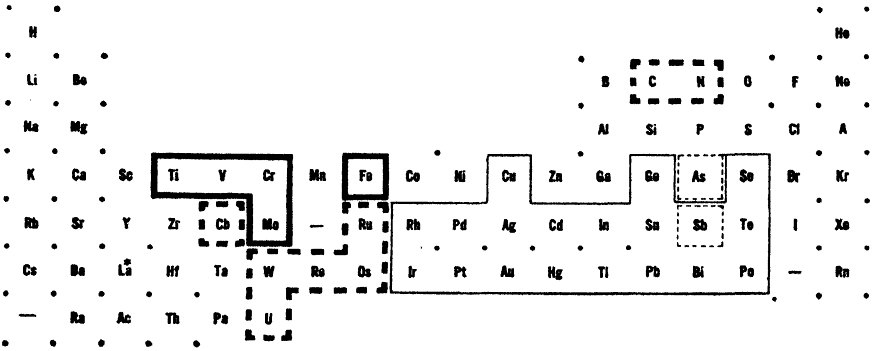
Heavy broken blocks inclose elements that are incompletely precipitated and yield soluble compounds of indefinite valence.

Light solid blocks inclose elements that are precipitated as sulphides.

Light broken blocks inclose elements that may interfere as explained in the text.

TABLE 81

Reduction by Zinc in Diluted (5 + 100) Sulphuric Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71 (see text).

Heavy solid blocks inclose elements that are reduced to definite valences.

Heavy broken blocks inclose elements that are reduced to indefinite valences, or introduce uncertainties.

Light solid blocks inclose elements that are reduced to metal.

Light broken blocks inclose elements that form a gas.

slowly in cold and quite rapidly in hot solutions, from the trivalent to the sexivalent state.[3] If the preliminary treatment with $KMnO_4$ is omitted, selenium and tellurium are precipitated by hydrogen sulphide. On account of the color of their solutions, cobalt and nickel interfere if present in large amount.

IV. Reduction with Zinc and Sulphuric Acid

Treatment with zinc and sulphuric acid serves for the reduction of a number of elements. As shown in Table 81, some are reduced to a definite valence, some are reduced to an indefinite stage, some are reduced to the metallic state, and some form gases.

Reductions of the first type proceed to the bivalent state with iron, vanadium, and chromium, and to the trivalent state with titanium and molybdenum. Reductions of the second type proceed nearly to the trivalent state with columbium, tungsten, and uranium, and nearly, if not completely, to the univalent (-1) state with rhenium. Reductions of these two types are often used in volumetric determinations of the elements concerned, for the reduced compounds can be reoxidized by adding measured volumes of solutions, such as standard solutions of potassium permanganate, of known oxidizing power. For such purposes, reductions are usually made in a Jones reductor. This consists essentially of a glass tube containing a column of amalgamated zinc, through which the acid solution of the compound can be drawn. Elements that would be reduced to metal and foul the zinc in the reductor are removed by a preliminary treatment with unamalgamated zinc in a beaker. Except with iron and uranium, it is necessary to protect the reduced compounds from air, for they are very susceptible of oxidation. These solutions are therefore usually caught under a solution containing ferric sulphate, which oxidizes the reduced compound to a more stable state and yields a reducing equivalent of the comparatively stable ferrous sulphate. The following equations serve to illustrate the reactions involved in determinations of elements by the procedures under discussion:

$$2\,H_3VO_4 + 3\,Zn + 5\,H_2SO_4 = 2\,VSO_4 + 3\,ZnSO_4 + 8\,H_2O$$

$$2\,VSO_4 + 2\,Fe_2(SO_4)_3 + 2\,H_2O = V_2O_2(SO_4)_2 + 4\,FeSO_4 + 2\,H_2SO_4$$

$$\begin{aligned}5\,V_2O_2(SO_4)_2 + 20\,FeSO_4 + 6\,KMnO_4 + 9\,H_2SO_4 + 6\,H_2O &= \\ 10\,H_3VO_4 + 10\,Fe_2(SO_4)_3 + 3\,K_2SO_4 + 6\,MnSO_4.\end{aligned}$$

That the consumption of permanganate per unit of vanadium ($6\,KMnO_4$ per 10 V) is not changed as a result of catching the reduced vanadium in a solution of ferric sulphate can be seen from the equation representing direct oxidation:

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[3] For a more detailed description of the method, see G. E. F. Lundell and H. B. Knowles, J. Am. Chem. Soc., **43**, 1560 (1921).

$$10\ VSO_4 + 6\ KMnO_4 + 16\ H_2O = 10\ H_3VO_4 + 3\ K_2SO_4 + 6\ MnSO_4 + H_2SO_4.$$

It is evident that an element cannot be determined in this manner unless other elements that cause consumption of permanganate either are absent or cause an effect that can be calculated. If the effect cannot be calculated, as with certain compounds of carbon or nitrogen or with titrations involving cerium or chromium in warm solutions, the interfering element must be removed before the determination is attempted.

Elements that are reduced to indefinite valences present special problems, columbium and tungsten requiring the use of empirical titers for the oxidizing solution, and uranium requiring special treatment of the reduced solution before it is titrated. Reduction of rhenium proceeds to the univalent (−1) state if solutions are dilute, ice-cold, and protected from oxygen. In the short time that the solution is in contact with the metallic zinc in a Jones reductor, ruthenium and osmium are reduced in part to metal and in part to compounds that consume potassium permanganate. Rhodium and iridium are also incompletely reduced to metal, but yield no intermediate compounds that consume permanganate. Because of the color of their solutions, cobalt and nickel interfere if present in large amount.

Reactions in which the elements are reduced to the metallic state are chiefly used to separate them from other elements, although sometimes the reactions serve for quantitative determinations. For either purpose, other reductants are more often used, as in separations of copper and cadmium from zinc by reduction with aluminum and sulphuric acid, or in determinations of gold and selenium by reduction with sulphur dioxide in hydrochloric acid solution.

Of the two elements that form gases, arsenic can be quantitatively converted to the extremely poisonous gas arsine, AsH_3, while antimony yields mostly metal, together with a small amount of the poisonous gas stibine, SbH_3. The reaction with arsenic serves for its detection, and for its determination when present in small amount. The reaction with antimony is chiefly of interest because of its effect on the tests for arsenic.

Europium can be reduced to the bivalent state by reduction with zinc in hydrochloric acid solution. The reduced compound can be oxidized by titration with iodine, or precipitated as an insoluble sulphate.

CHAPTER XXXVIII

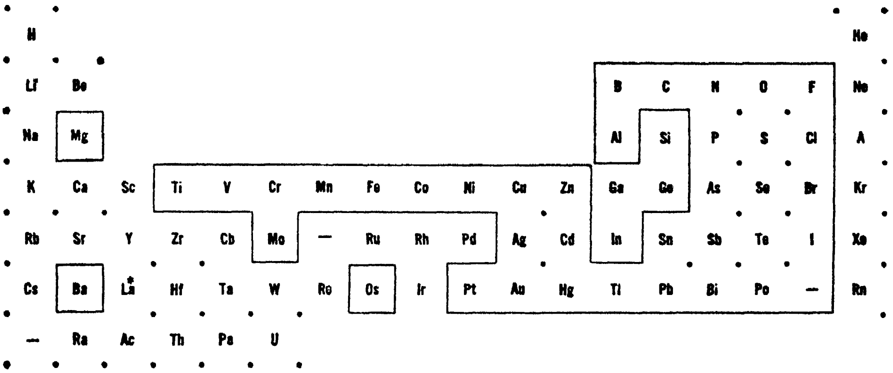
IODIMETRY, IODOMETRY, AND SIMILAR METHODS

A very important branch of oxidation-reduction methods is that which concerns titrations involving free halogens or compounds that can yield free halogens.

Generally speaking, the term iodimetry covers titrations with iodine, and iodometry covers titrations of iodine. In the same general class are methods involving the use of iodates, iodate and iodide, bromate, bromate and bromide, chlorine, bromine, hypochlorites, hypobromites, chloramine, and the like. These methods embrace a wide range of reactions and serve for the determination of a large number of elements. The wide applicability of such procedures is illustrated in Table 82.

TABLE 82

Elements That Can Be Determined by Iodometric Procedures



* Includes elements 58–71, excepting Ce Eu

Elements inclosed in blocks are those for which one or more iodometric methods of determination have been recommended.

The table, and the sections that follow, emphasize the fact that the analyst should not proceed with a determination of a given substance by an iodometric method unless he has convinced himself of the absence of the other substances that enter into the reactions in question.

Iodimetric and iodometric procedures can be grouped in two broad classes: (1) methods depending on the consumption of iodine, and (2) methods depending on the liberation of iodine. The former are used in determinations of substances that yield definite products when oxidized by iodine; the latter, in determinations of oxidized substances that can be made to enter into reactions that yield iodine. Final titrations are always performed in neutral (pH 7) or acid ($p\text{H} < 7$) solutions.

A. Methods Depending on the Consumption of Iodine

In volumetric processes involving oxidation by iodine, the iodine can be added in the form of a standard solution containing iodine and potassium iodide, or potassium iodate and potassium iodide. The latter are quite stable and yield iodine when treated with acid

$$KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2.$$

Solutions of iodine are less stable but are of more general application, for iodate-iodide solutions cannot be used if the titration must be made in solutions that are neutral or of very low acidity. In iodine solutions, potassium iodide serves the threefold purpose of aiding in the solution of the iodine, lowering its vapor pressure so that danger of loss by volatilization is lessened, and giving a sharper end point, if this is determined by using starch. In iodate solutions, the most important function of the iodide is to furnish the iodine for the reaction.

Standard solutions of either type can be prepared by dissolving a weighed amount of pure iodine or iodate in a solution of potassium iodide, and diluting to definite volume. More often, the solution is standardized either by (1) the use of a pure chemical such as arsenious oxide, (2) the use of a standard solution such as one of sodium thiosulphate, or (3) titration of a solution of a material which is of known purity and has been carried through all steps of the method in which the standardized solution is to be used.

The completion of the reaction with iodine is usually judged by adding a solution of starch and titrating until the solution is permanently tinted by the characteristic blue compound which free iodine forms with starch, although there is an increasing tendency to follow such titrations potentiometrically (page 163).

Methods depending on the consumption of iodine can be divided into three general subclasses as follows:

I. DIRECT TITRATION IN NEUTRAL OR FEEBLY ACID SOLUTIONS

Some of the compounds that can be oxidized by iodine in acid solutions are not entirely stable in the presence of the hydriodic acid that is formed, as for example

$$H_3AsO_3 + H_2O + I_2 \rightleftarrows H_3AsO_4 + 2\,HI$$

Titrations of such compounds must be made in the presence of substances that will neutralize the hydriodic acid without interfering in any way with the course of the reaction. With arsenic this is done by titrating in a 0.12

molar solution of sodium bicarbonate saturated with carbon dioxide

$$Na_2HAsO_3 + 2\,NaHCO_3 + I_2 = Na_2HAsO_4 + 2\,NaI + H_2O + 2\,CO_2.$$

The guiding consideration in using the neutralizing medium is that it shall not render the solution so alkaline that iodine is consumed in forming hypoiodous acid

$$I_2 + H_2O = HIO + HI$$

or hypoiodite and iodide

$$I_2 + 2\,NaOH = NaIO + NaI + H_2O.$$

Procedures of the same general character as that used for arsenic also serve for the determination of antimony

$$Na_2HSbO_3 + 2\,NaHCO_3 + I_2 = Na_2HSbO_4 + 2\,NaI + H_2O + CO_2$$

and cyanides

$$KCN + KOH + CO_2 + I_2 = ICN + KI + KHCO_3.$$

II. DIRECT TITRATION IN SOLUTIONS OF HIGH ACIDITY

If compounds formed by oxidation with iodine are not susceptible of reduction by hydriodic acid, there is no need for its neutralization, and so titrations can be made in solutions that contain notable amounts of acid. Examples of procedures of this type are those used in determinations of sulphides

$$ZnS + 2\,HCl + I_2 = S + 2\,HI + ZnCl_2$$

thiosulphates

$$2\,Na_2S_2O_3 + 4\,HCl + I_2 = H_2S_4O_6 + 2\,HI + 4\,NaCl$$

and tin

$$SnCl_2 + 2\,HCl + I_2 = SnCl_4 + 2\,HI.$$

III. INDIRECT TITRATION METHODS

Some oxidations by means of iodine are not satisfactory unless an excess of iodine is used. More than enough of a standard solution of iodine is added in measured volume, and then the excess is determined by titrating with a standard solution of sodium thiosulphate or arsenite under suitable conditions. Examples of such procedures are those used in the determination of sulphides

$$4\,I_2\text{ (plus excess)} + 2\,HCl + 4\,H_2O + Na_2S = H_2SO_4 + 2\,NaCl + 8\,HI + \text{excess of } I_2$$

sulphites

$$I_2 \text{ (plus excess)} + 2\,HCl + H_2O + Na_2SO_3 = H_2SO_4 + 2\,NaCl + 2\,HI + \text{excess of } I_2$$

formaldehyde

$$HCHO + I_2 \text{ (plus excess)} + 3\,NaOH = NaCOOH + 2\,NaI + 2\,H_2O + \text{excess of } I_2$$

and mercurous chloride

$$2\,HgCl + 6\,KI + I_2 \text{ (plus excess)} = 2\,K_2HgI_4 + 2\,KCl + \text{excess of } I_2.$$

In titrations of this type it is desirable that all the standard solutions be of equivalent strength, so that volumes can be subtracted from one another directly in order to arrive at the volume of the iodine solution required in the main reaction.

B. Methods Depending on the Liberation of Iodine

Of iodometric methods, those which depend on the liberation of iodine are by far the most numerous and show the greatest variety. The liberated iodine is titrated with standard solutions suited to the conditions. Usually the final solutions are quite acid, and titrations are made with sodium thiosulphate. Titrations with standard solutions of sodium arsenite are confined to reactions that can be performed in buffered solutions of very low acidity.

The different subgroups of methods in which iodine is liberated are outlined in the following sections.

I. Liberation of Iodine by Direct Replacement with Chlorine or Bromine

Methods involving the liberation of iodine by direct replacement are those in which free chlorine or bromine must be determined. These depend on the well-known reactions

$$2\,KI + Cl_2 = 2\,KCl + I_2$$
$$2\,KI + Br_2 = 2\,KBr + I_2.$$

II. Liberation of Iodine by Treatment with Potassium Iodide and Hydrochloric or Sulphuric Acid

If reactions between an oxidizing compound and hydriodic acid proceed rapidly and quantitatively at ordinary temperatures, the liberated iodine can be titrated directly. Examples of such reactions are:

$$O_3 + 2\,KI = KIO + KI + O_2$$
$$KIO + KI + H_2SO_4 = K_2SO_4 + H_2O + I_2$$
$$O_2 + 4\,KI + (NO_2) + 4\,HCl = 4\,KCl + 2\,H_2O + (NO_2) + 2\,I_2$$

$$\mathrm{H_2O_2 + 2\,KI + H_2SO_4 = K_2SO_4 + 2\,H_2O + I_2}$$

$$\mathrm{2\,CeO_2 + 2\,KI + 8\,HCl = 2\,CeCl_3 + 2\,KCl + 4\,H_2O + I_2}$$

$$\mathrm{2\,Co(OH)_3 + 2\,KI + 6\,HCl = 2\,CoCl_2 + 2\,KCl + 6\,H_2O + I_2}$$

$$\mathrm{2\,Ni(OH)_3 + 2\,KI + 6\,HCl = 2\,NiCl_2 + 2\,KCl + 6\,H_2O + I_2}$$

$$\mathrm{HClO + 2\,KI + HCl = 2\,KCl + H_2O + I_2}$$

$$\mathrm{H_2SeO_3 + 4\,KI + 4\,HCl = Se + 4\,KCl + 3\,H_2O + 2\,I_2}$$

$$\mathrm{2\,H_2CrO_4 + 6\,KI + 12\,HCl = 2\,CrCl_3 + 6\,KCl + 8\,H_2O + 3\,I_2}$$

$$\mathrm{HBrO_3 + 6\,KI + 5\,HCl = 5\,KCl + KBr + 3\,H_2O + 3\,I_2}$$

$$\mathrm{HIO_3 + 5\,KI + 5\,HCl = 5\,KCl + 3\,H_2O + 3\,I_2}$$

$$\mathrm{HClO_3 + 6\,KI + 5\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2}$$

$$\mathrm{2\,KMnO_4 + 10\,KI + 16\,HCl = 12\,KCl + 2\,MnCl_2 + 8\,H_2O + 5\,I_2}$$

$$\mathrm{KIO_4 + 7\,KI + 8\,HCl = 8\,KCl + 4\,H_2O + 4\,I_2}$$

$$\mathrm{2\,KNO_2 + 2\,H_2SO_4 + 2\,KI = 2\,K_2SO_4 + 2\,NO + 2\,H_2O + I_2}$$

$$\mathrm{SbCl_5 + 2\,KI + (HCl) = SbCl_3 + 2\,KCl + (HCl) + I_2}$$

$$\mathrm{2\,FeCl_3 + 2\,KI + (HCl) = 2\,FeCl_2 + 2\,KCl + (HCl) + I_2}$$

$$\begin{aligned}&\mathrm{2\,K_3Fe(CN)_6 + 2\,KI + 2\,HCl + 3\,ZnSO_4 + 2\,NaHCO_3 =}\\ &\qquad \mathrm{K_2Zn_3[Fe(CN)_6]_2 + 3\,K_2SO_4 + 2\,NaCl + 2\,H_2O + 2\,CO_2 + I_2.}\end{aligned}$$

It is obvious that a number of other compounds, such as peroxides, oxidizing acids, and their salts can also be determined in the same fashion. Some reactions proceed slowly or do not go to completion at room temperature, but do proceed quantitatively if the solution is boiled. In such case the distillate is caught in a solution of potassium iodide, which serves the dual purpose of aiding in the solution of the iodine and of rendering it less volatile. Examples of such procedures are

$$\mathrm{2\,MoO_3 + 4\,KI + 4\,HCl = 2\,MoO_2I + 4\,KCl + 2\,H_2O + I_2}$$

$$\mathrm{H_3SbO_4 + 2\,KI + 5\,HCl = SbCl_3 + 2\,KCl + 4\,H_2O + I_2}$$

$$\mathrm{2\,H_3VO_4 + 2\,KI + 6\,HCl = 2\,VOCl_2 + 2\,KCl + 6\,H_2O + I_2.}$$

The same procedure can, of course, be employed in determinations of most of the substances that yield iodine at room temperature.

III. Liberation of Iodine by Treatment with Potassium Iodide and Potassium Iodate

Solutions containing potassium iodide and potassium iodate yield iodine if they are treated with substances that increase their concentration of hydrogen ions. This behavior forms the basis for the determination of the stronger acids when they occur by themselves

$$\mathrm{KIO_3 + 5\,KI + 6\,HCl = 6\,KCl + 3\,H_2O + 3\,I_2}$$

$$\mathrm{KIO_3 + 5\,KI + 3\,H_2SO_4 = 3\,K_2SO_4 + 3\,H_2O + 3\,I_2}$$

or of bases that form salts which are of definite composition and which can be made to hydrolyze completely

$$K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24\ H_2O + KIO_3 + 5\ KI = 2\ Al(OH)_3 + 4\ K_2SO_4 + 21\ H_2O + 3\ I_2.$$

Somewhat different in its purpose, but along the same lines, is the interesting method by which boric acid can be freed from acidic substances that would interfere in its titration, as follows

$$H_3BO_3 + 4\ HCl + H_2CO_3 + BaCl_2 + KIO_3 + 5\ KI = H_3BO_3 + 6\ KCl + 3\ H_2O + BaCO_3 + 3\ I_2$$

in which the barium chloride is added to remove carbonic acid, and the iodate-iodide serves to remove the mineral acid, whether free or present as an easily hydrolyzed salt. In these reactions barium chloride does not hydrolyze, and boric acid is too weak to react with the iodate-iodide mixture. The free iodine is removed by adding a solution of starch and titrating with a solution of thiosulphate

$$3\ I_2 + 6\ Na_2S_2O_3 = 3\ Na_2S_4O_6 + 6\ NaI$$

after which the boric acid can be titrated as usual with sodium hydroxide after adding mannitol and phenolphthalein.

IV. Liberation of Iodine by Precipitation

Precipitation reactions which result in the liberation of iodine are of two kinds, those in which iodine is liberated by direct action, and those in which the liberation of iodine follows a preliminary precipitation. In either type, the amount of iodine obtained is determined by direct titration, and is an index of the substance sought. Examples of the first type are

$$2\ Cu(C_2H_3O_2)_2 + 4\ KI = 2\ CuI + 4\ KC_2H_3O_2 + I_2$$

and

$$AuCl_3 + 3\ KI = AuI + 3\ KCl + I_2.$$

Reactions of the second type apply to elements which can be made to form insoluble chromates of definite composition. The chromate is separated by filtration, washed, and treated with potassium iodide and hydrochloric acid. The iodine obtained then furnishes, of course, an index of the element in question, as for example

$$Pb(C_2H_3O_2)_2 + K_2CrO_4 = PbCrO_4 + 2\ KC_2H_3O_2$$

$$PbCrO_4 + 2\ HCl = PbCl_2 + H_2CrO_4$$

$$2\ H_2CrO_4 + 6\ KI + 12\ HCl = 2\ CrCl_3 + 6\ KCl + 8\ H_2O + 3\ I_2$$

in which 3 atoms of iodine represent 1 atom of lead. Similar procedures can be followed in determinations of barium, bismuth, and silver.

Along the same lines, though somewhat different in principle, is the determination of the sulphate ion. In this method, the sulphate ion is precipitated by adding an acid solution of barium chromate in excess

$$K_2SO_4 + [BaCl_2 + H_2CrO_4 + HCl] \text{ plus an excess } = BaSO_4 + 2\,KCl + HCl + H_2CrO_4 + \text{excess of } [BaCl_2 + H_2CrO_4 + HCl]$$

the excess of barium ion is reprecipitated as chromate by adding ammonium hydroxide

$$BaSO_4 + 2\,KCl + HCl + H_2CrO_4 + [BaCl_2 + H_2CrO_4 + HCl] + 6\,NH_4OH = BaSO_4 + BaCrO_4 + 2\,KCl + 4\,NH_4Cl + 6\,H_2O + (NH_4)_2CrO_4$$

after which the precipitated barium sulphate and barium chromate are removed by filtration, and the filtrate is treated with potassium iodide and hydrochloric acid to react with the ammonium chromate

$$2\,(NH_4)_2CrO_4 + 6\,KI + 16\,HCl = 6\,KCl + 2\,CrCl_3 + 4\,NH_4Cl + 8\,H_2O + 3\,I_2$$

which was formed by the reaction between the potassium sulphate and the acid solution of barium chromate at the start of the determination.

V. LIBERATION OF IODINE THROUGH CHLORINE OR BROMINE

In quite a few iodometric processes the oxidized material is treated with hydrochloric or hydrobromic acid, the halogen that is formed is distilled and caught in a solution of potassium iodide, and the iodine then titrated as usual. Such treatments can be applied to most of the materials that yield iodine as listed in II. The following reactions are typical

$$2\,HNO_3 + (MnCl_2) + 6\,HCl = (MnCl_2) + 4\,H_2O + 2\,NO + 3\,Cl_2$$

$$2\,H_3VO_4 + 2\,KBr + 6\,HCl = 2\,VOCl_2 + 2\,KCl + 6\,H_2O + Br_2$$

$$H_2SeO_4 + 2\,HCl = H_2SeO_3 + H_2O + Cl_2$$

$$MnO_2 + 4\,HCl = MnCl_2 + 2\,H_2O + Cl_2$$

$$K_2TeO_4 + 4\,HCl = 2\,KCl + H_2TeO_3 + H_2O + Cl_2.$$

C. Methods Depending on the Use of Iodates

Solutions which contain iodates alone (as contrasted with those containing both iodate and iodide) can be used in titrations of iodine

$$2\,I_2 + 6\,HCl + KIO_3 = 5\,ICl + KCl + 3\,H_2O$$

of iodides

$$2\,KI + 6\,HCl + KIO_3 = 3\,ICl + 3\,KCl + 3\,H_2O$$

or of certain reducing substances, such as arsenious acid

$$2\,H_3AsO_3 + 2\,HCl + KIO_3 = 2\,H_3AsO_4 + ICl + KCl + H_2O.$$

Iodine monochloride, ICl, which is formed in such titrations is brownish yellow, and cannot exist in solution as long as any reducing compound is present.

Titrations of iodine by solutions of potassium iodate must be made in rather strong acid, as for example 4 to 6 *N* hydrochloric acid. The same is true of titrations of iodides or other reducing substances in which all the iodine is to be converted to the monochloride. If weaker acid is used, say 0.1 to 2.0 *N* hydrochloric acid, titrations can be stopped at the point at which the iodate has been reduced to iodine

$$5\ KI + 6\ HCl + KIO_3 = 3\ I_2 + 6\ KCl + 3\ H_2O$$

$$5\ H_3AsO_3 + 2\ HCl + 2\ KIO_3 = I_2 + 5\ H_3AsO_4 + 2\ KCl + H_2O.$$

Finally, if oxidations of reducing substances are made in weak acid solutions, say 0.1 to 2.0 *N* hydrochloric acid, containing mercuric sulphate, the titrations can be stopped at the point at which the iodate has been reduced to iodide

$$12\ H_3AsO_3 + 4\ KIO_3 + HgSO_4 + (HCl) = 12\ H_3AsO_4 + K_2HgI_4 + K_2SO_4 + (HCl)$$

for the iodide is converted to the fairly stable complex ion $[HgI_4]$ as fast as it is formed.[1]

The stage at which potassium iodate has been converted to iodide, iodine, or iodine monochloride can be detected potentiometrically (page 164). The stage at which conversion to the monochloride is complete can also be detected by adding chloroform or carbon tetrachloride to the solution, and titrating until the purple color imparted by free iodine is destroyed.

Typical determinations based on direct oxidation with iodate are the following:

$$Mo_2O_3 + 2\ HCl + KIO_3 = Mo_2O_5 + KCl + H_2O + ICl$$

$$2\ H_3AsO_3 + 2\ HCl + KIO_3 = 2\ H_3AsO_4 + KCl + H_2O + ICl$$

$$2\ H_2SO_3 + 2\ HCl + KIO_3 = 2\ H_2SO_4 + KCl + H_2O + ICl$$

$$Na_2S_2O_3 + 2\ HCl + 2\ KIO_3 = Na_2SO_4 + K_2SO_4 + H_2O + 2\ ICl$$

$$2\ Na_2S_4O_6 + 10\ HCl + 7\ KIO_3 = 2\ Na_2SO_4 + 2\ K_2SO_4 + 4\ H_2SO_4 + 3\ KCl + H_2O + 7\ ICl$$

$$4\ HgCl + 6\ HCl + KIO_3 = 4\ HgCl_2 + KCl + 3\ H_2O + ICl$$

$$2\ SnCl_2 + 6\ HCl + KIO_3 = 2\ SnCl_4 + KCl + 3\ H_2O + ICl$$

$$2\ SbCl_3 + 6\ HCl + KIO_3 = 2\ SbCl_5 + KCl + 3\ H_2O + ICl$$

$$4\ CuCNS + 14\ HCl + 7\ KIO_3 = 4\ CuSO_4 + 7\ KCl + 4\ HCN + 5\ H_2O + 7\ ICl$$

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[1] See G. F. Smith, J. Am. Chem. Soc., **45**, 1417 (1923), I. C. Schoonover and N. H. Furman, ibid., **55**, 3123 (1933), and N. H. Furman and C. O. Miller, ibid., **59**, 152, 161, (1937).

$$HgZn(CNS)_4 + 12\,HCl + 6\,KIO_3 = HgSO_4 + ZnSO_4 + 2\,H_2SO_4 + 6\,KCl + 4\,HCN + 2\,H_2O + 6\,ICl$$

$$N_2H_4 \cdot H_2SO_4 \text{ (hydrazine sulphate)} + 2\,HCl + KIO_3 = N_2 + KCl + H_2SO_4 + 3\,H_2O + ICl.$$

As iodate solutions react with iodine, it is apparent that they can be used in determinations of substances that can be made to enter into reactions yielding definite amounts of iodine. This, then, opens the field to determinations of *oxidizing* as well as *reducing* substances. The chief difficulty in such titrations is that provision must be made for the potassium iodide that is usually present. This is done by adding an excess of a standard solution of the iodide, acidifying strongly, and then titrating the excess of iodide as well as the iodine by means of a standard solution of potassium iodate. The latter is preferably of such strength that 1 ml will oxidize exactly 1 ml of the iodide solution, for then the difference between the volumes of iodide and iodate solutions that are used represents one-half of the volume of the potassium iodide solution needed in the reaction with the oxidizing substance. This follows because the iodine formed requires only one-half as much iodate as the iodide from which it was derived

$$2\,I_2 + 6\,HCl + KIO_3 = KCl + 3\,H_2O + 5\,ICl$$

$$4\,KI + 12\,HCl + 2\,KIO_3 = 6\,KCl + 6\,H_2O + 6\,ICl.$$

Examples of such determinations are those of PbO_2, MnO_2, BaO_2, $KMnO_4$, $K_2Cr_2O_7$, and most of the other compounds that yield iodine as described in B, I and II.

D. Methods Depending on the Use of Bromates

Titrations which depend on oxidation by bromate in acid solution can be made with solutions containing potassium bromate alone or in conjunction with potassium bromide.

I. TITRATIONS WITH SOLUTIONS OF POTASSIUM BROMATE

Solutions containing bromate alone can be used in titrations in which the bromate is reduced to bromide

$$6\,CuCl + 6\,HCl + KBrO_3 = 6\,CuCl_2 + 3\,H_2O + KBr$$

or to bromine

$$5\,KBr + 6\,HCl + KBrO_3 = 6\,KCl + 3\,H_2O + 3\,Br_2.$$

Determinations which depend on the reduction of the bromate to bromide are of two types: (1) titrations which are stopped as soon as enough of the standard bromate solution has been added to complete the oxidation, and (2) titrations in which more than enough of the bromate solution is added, and the excess then determined by adding potassium iodide and titrating the resultant iodine with a standard solution of sodium thiosulphate.

In titrations of the first type, as for example with antimony, the stage at which all the compound has been oxidized

$$3\ SbCl_3 + KBrO_3 + 9\ H_2O = 3\ H_3SbO_4 + 9\ HCl + KBr$$

can be detected by using a colored organic compound, such as methyl orange, whose color is destroyed by the liberated bromine

$$5\ KBr + 6\ HCl + KBrO_3 = 6\ KCl + 3\ H_2O + 3\ Br_2$$

as soon as oxidation is complete. The completion of the reaction can also be detected by potentiometric methods.

The applicability of such methods is illustrated by the following:

$$6\ TiCl_3 + 6\ HCl + KBrO_3 = 6\ TiCl_4 + 3\ H_2O + KBr$$

$$6\ K_4Fe(CN)_6 + 6\ HCl + KBrO_3 = 6\ K_3Fe(CN)_6 + 6\ KCl + 3\ H_2O + KBr$$

$$3\ N_2H_4 + 2\ KBrO_3 = 3\ N_2 + 6\ H_2O + 2\ KBr$$

$$3\ SnCl_2 + 6\ HCl + KBrO_3 = 3\ SnCl_4 + 3\ H_2O + KBr$$

$$3\ Tl_2SO_4 + 6\ H_2SO_4 + 2\ KBrO_3 = 3\ Tl_2(SO_4)_3 + 6\ H_2O + 2\ KBr$$

$$3\ Na_2HAsO_3 + 6\ HCl + KBrO_3 = 3\ H_3AsO_4 + 6\ NaCl + KBr$$

$$6\ FeCl_2 + 6\ HCl + KBrO_3 = 6\ FeCl_3 + 3\ H_2O + KBr.$$

Titrations in which an excess of the standard solution is added, as in determinations of oxalic acid, are usually made in solutions which are moderately acid, 0.2 *N*–1 *N*, and contain a mercuric salt that forms a stable complex ion with the bromide[1]

$$12\ H_2C_2O_4 + 4\ KBrO_3\ \text{(plus excess)} + Hg(ClO_4)_2 =$$
$$24\ CO_2 + 12\ H_2O + K_2HgBr_4 + 2\ KClO_4 + \text{excess of}\ KBrO_3.$$

When reaction is complete, the solution is treated with potassium iodide in excess

$$KBrO_3 + 6\ KI + 6\ HCl = KBr + 6\ KCl + 3\ H_2O + 3\ I_2$$

and then titrated with a standard solution of sodium thiosulphate

$$I_2 + 2\ Na_2S_2O_3 = 2\ NaI + Na_2S_4O_6.$$

Typical applications are the following:

$$3\ Mn(NO_3)_2 + 3\ H_2O + KBrO_3 = 3\ MnO_2 + 6\ HNO_3 + KBr$$

$$2\ Cr(NO_3)_3 + 5\ H_2O + KBrO_3 = 2\ H_2CrO_4 + 6\ HNO_3 + KBr$$

$$3\ HNO_2 + KBrO_3 = 3\ HNO_3 + KBr$$

$$3\ SnCl_2 + 6\ HCl + KBrO_3 = 3\ SnCl_4 + 3\ H_2O + KBr.$$

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[1] See G. F. Smith, J. Am Chem. Soc., **45**, 1417 (1923), I. C. Schoonover and N. H. Furman, ibid., **55**, 3123 (1933), and N. H. Furman and C. O. Miller, ibid., **59**, 152, 161, (1937).

In a variation of this method measured volumes of three standard solutions are used, first a solution of potassium bromate (A) which is added in excess, then more than enough (B) of a standard solution of sodium oxalate or ferrous sulphate to destroy the excess of bromate, and finally just enough (C) of a standard solution of potassium permanganate to react with the excess of oxalate or sulphate. Thus, in a determination of nitrous acid the reactions are:

$$12\ HNO_2 + 4\ KBrO_3\ \text{(plus excess)} + Hg(ClO_4)_2 = 12\ HNO_3 + K_2HgBr_4 + 2\ KClO_4 + \text{(excess of } KBrO_3)$$

$$4\ KBrO_3 + 24\ FeSO_4\ \text{(plus excess)} + 12\ H_2SO_4 + Hg(ClO_4)_2 = 12\ Fe_2(SO_4)_3 + K_2HgBr_4 + 2\ KClO_4 + 12\ H_2O + \text{(excess of } FeSO_4)$$

$$10\ FeSO_4 + 8\ H_2SO_4 + 2\ KMnO_4 = 5\ Fe_2(SO_4)_3 + K_2SO_4 + 2\ MnSO_4 + 8\ H_2O.$$

It is obvious that, if the three solutions are of exactly the same strength, the volume of bromate solution required in the oxidation of the nitrous acid is represented by A − (B − C).

Determinations depending on the reduction of bromate to bromine are made by adding a standard solution of potassium bromate in excess to solutions of moderate acidity, 2 *N* nitric or perchloric acid, boiling for 5–10 minutes to expel the bromine, and then adding an excess of potassium iodide to the solution and titrating with a standard solution of sodium thiosulphate as already described.

Such treatments can be applied in determinations of any of the substances that have been discussed in this section provided that (1) no mercuric salt is added, and (2) hydriodic acid is without effect on the oxidized compounds. In determinations of tin, for example, the oxidation of the tin is represented by the reaction

$$5\ SnCl_2 + 12\ HClO_4 + 2\ KBrO_3\ \text{(plus excess)} = 2\ SnCl_4 + 3\ Sn(ClO_4)_4 + 2\ KCl + 6\ H_2O + \text{(excess of } KBrO_3) + Br_2.$$

In some modifications of the method, as for example in the determination of potassium bromide occurring in potassium bromate, the distilled bromine can be collected in a solution of potassium iodide, and the resulting iodine titrated.

II. SOLUTIONS CONTAINING BROMATE AND BROMIDE

Standard solutions containing bromate and bromide, or standard solutions of bromate used in conjunction with added bromide, furnish a convenient source of bromine in reactions that proceed best in its presence, as for example in determinations of sulphides

$$3\ Na_2S + 4\ KBrO_3 + 20\ KBr + 24\ HCl = 3\ Na_2SO_4 + 24\ HBr + 24\ KCl$$

thiocyanates

$$\mathrm{HCNS + KBrO_3 + 5\ KBr + 6\ HCl + H_2O = H_2SO_4 + HCN + 6\ HBr + 6\ KCl}$$

8-hydroxyquinoline

$$\mathrm{3\ C_9H_7NO + 2\ KBrO_3 + 10\ KBr + 12\ HCl = 3\ C_9H_5Br_2NO + 6\ HBr + 12\ KCl + 6\ H_2O}$$

and phenol

$$\mathrm{C_6H_5OH + KBrO_3 + 5\ KBr + 6\ HCl = C_6H_2Br_3OH + 3\ HBr + 6\ KCl + 3\ H_2O.}$$

In each of the above reactions the standard solution is added in excess. This yields an excess of bromine

$$\mathrm{KBrO_3 + 5\ KBr + 6\ HCl = 6\ KCl + 3\ H_2O + 3\ Br_2}$$

which is determined by converting it to iodine after the reaction is complete

$$\mathrm{3\ Br_2 + 6\ KI = 6\ KBr + 3\ I_2}$$

and titrating with thiosulphate

$$\mathrm{3\ I_2 + 6\ Na_2S_2O_3 = 6\ NaI + 3\ Na_2S_4O_6.}$$

E. Methods Depending on the Use of Bromine, Chlorine, Hypobromites, Hypochlorites, and Chloramine $\left(\mathrm{CH_3C_6H_4SO_2N}\left\langle\begin{matrix}\mathrm{Cl}\\ \mathrm{Na}\end{matrix}\right.\right)$

From what has been said in the preceding sections it will be evident that solutions of bromine, chlorine, hypobromites, hypochlorites, or compounds such as chloramine can also be used in volumetric processes. Some of these applications are indicated in the following:

$$\mathrm{3\ Br_2 + C_6H_5NH_2 = C_6H_2Br_3NH_2 + 3\ HBr}$$

$$\mathrm{Cl_2 + KCN = ClCN + KCl}$$

$$\mathrm{KBrO + Na_2HAsO_3 = Na_2HAsO_4 + KBr}$$

$$\mathrm{NaClO + H_2O_2 = H_2O + O_2 + NaCl}$$

$$\mathrm{CH_3C_6H_4SO_2N}\left\langle\begin{matrix}\mathrm{Na}\\ \mathrm{Cl}\end{matrix}\right. \mathrm{+ SnCl_2 + 2\ HCl = SnCl_4 + CH_3C_6H_4SO_2NH_2 + NaCl.}$$

CHAPTER XXXIX

POTENTIOMETRIC METHODS

As stated in the preceding chapters, the end points of most analytical reactions involving oxidation, reduction, neutralization, or precipitation can be determined potentiometrically if suitable apparatus is available and proper conditions can be established. For many of the simpler titrations, the apparatus need not be complicated or costly. Very little extra equipment is needed for setting up a simple potentiometric device if there are available in the laboratory: (1) a 16-inch Jagabi slide-wire type of rheostat (800–1000 Ω and 0.6–0.7 ampere) to which a 40-cm rule can be clamped; (2) a beaker in which to make the titration; (3) an ordinary dry cell; (4) a platinum electrode for oxidation reactions, or a piece of antimony foil or wire for certain neutralization reactions; (5) a battery switch and tapping key; (6) a galvanometer (Leeds & Northrup pointer type No. 2320 is satisfactory); (7) some stirring device; and (8) a calomel, a silver-silver chloride, or other suitable reference electrode. Beyond this simple assembly of parts more and more complicated devices can be introduced, almost without limit, but it should be remembered that all the apparatus is required to do is to show the change in potential that occurs when a reaction has been made to go to completion. For example, in the titration of ferrous iron with ceric sulphate, the apparatus must show distinctly and definitely when the voltage jumps from the ferrous-ferric system (0.78 v) to that of the ceric-cerous system (1.45 v). See Table 76, electrode potentials. It is obvious that it is the relative and not the absolute change in the indicating potential that heralds the end of the reaction.

A. Electrode Systems

In the first or classical method, the potential difference between an *indicator electrode* and a *reference electrode*, such as the calomel half-cell, is measured during the course of the titration. The end point may be found by plotting the data (emf against milliliters of titrating solution) and determining the point of inflection of the curve.

In the second method, the end point is shown by an abrupt rise or fall in the external voltage of a cell in which two *metallic electrodes* are employed, thus eliminating the rather troublesome calomel half-cell. The various kinds of bimetallic electrode systems include platinum-platinum, platinum-gold, platinum-gold amalgam, platinum-copper amalgam, platinum-graphite, antimony-copper amalgam, bismuth-silver, tungsten-nickel, tungsten-copper, tungsten-cobalt, tungsten-silicon, and copper-copper oxide. Silicon carbide electrodes have also been used.

The third method depends upon titration to *zero difference of potential between the reference and indicator electrodes.* This method requires the preparation of a reference electrode that has the potential which the indicator electrode will have at the end point.

The fourth is the *differential titration method,* in which a concentration cell is formed from the solution under titration by keeping a small portion of the solution surrounding one of two similar electrodes from mixing with the main part until after each increment of the titrating solution is added. The end point is at the maximum potential difference, that is, where

$$\frac{\Delta \text{ emf}}{\text{increment of reagent added}} = \text{a maximum.}$$

The plotting of curves is unnecessary, and the calomel half-cell is eliminated. An obvious advantage of this method is that the two electrodes are always in solutions of almost identical composition.

The fifth or *polarized indicator electrode* method has not found wide application.

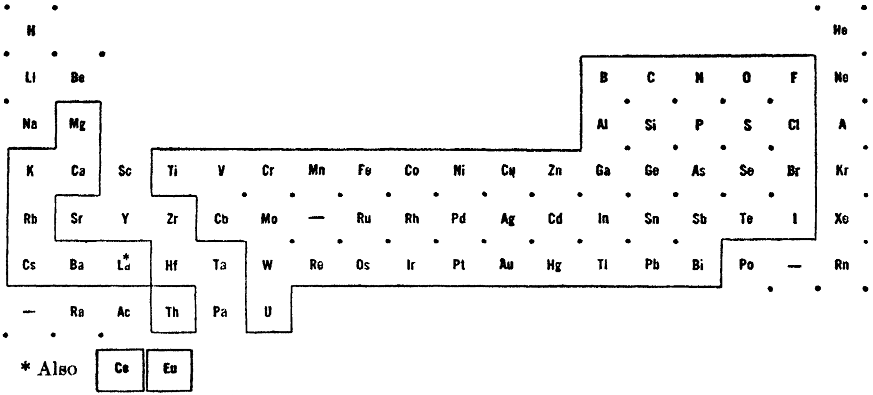
Various other combinations are in use. The hydrogen electrode is used as a reference electrode in some of the more fundamental determinations of hydrogen ions. In practical work, however, quinhydrone, antimony-air (oxygen), and glass electrodes are often substituted.

B. Applications of Potentiometric Methods

Table 83 and the incomplete tabulations shown in Table 84 illustrate the wide range of application of potentiometric methods. In addition to the reactions listed in Table 84, practically all titrations with acids and alkalies and also the reactions given in the chapter on Iodimetry, Iodometry, and Similar Methods, page 151, can be followed potentiometrically. The list is impressive and shows that many reactions for which none of the ordinary types of indicator are available at present can be easily studied potentiometrically. In fact, the studies of the newer oxidation-reduction and other indicators are based on potentiometric titrations. It is obvious that there may be numerous interferences in any given determination, and that frequently it will be necessary to remove certain elements before a determination can be made.

TABLE 83

Elements for Which Potentiometric Methods of Determination Have Been Recommended


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U
* Also Ce Eu

Elements inclosed in blocks are those for which one or more potentiometric methods of determination have been recommended.

TABLE 84

Potentiometric Titrations *

I. Potentiometric titrations that have been successfully made by oxidation with $KMnO_4$, $K_2Cr_2O_7$, or $Ce(SO_4)_2$.

(1) = reactions with $KMnO_4$ (2) = reactions with $K_2Cr_2O_7$
(3) = reactions with $Ce(SO_4)_2$

Substance determined	Partial reaction	Substance determined	Partial reaction
Antimony (1) (2) (3)	$\mathrm{Sb} \xrightarrow{+++} \mathrm{Sb}^{+++++}$	Manganese (presence of F⁻) (1)	$\mathrm{Mn} \xrightarrow{++} \mathrm{Mn}^{+++}$
Arsenic (2) (3)	$\mathrm{As} \xrightarrow{+++} \mathrm{As}^{+++++}$	Mercury (1) (3)	$\mathrm{Hg_2} \xrightarrow{++} 2\,\mathrm{Hg}^{++}$
Chromium (3)	$2\mathrm{Cr} \xrightarrow{+++} \mathrm{Cr_2O_7}^{--}$	Molybdenum (1)	$\mathrm{Mo} \xrightarrow{+++} \mathrm{Mo}^{++++++}$
Ferrocyanide (1) (2) (3)	$\mathrm{Fe(CN)_6} \xrightarrow{----} \mathrm{Fe(CN)_6}^{---}$	Molybdenum (1) (3)	$\mathrm{Mo} \xrightarrow{+++++} \mathrm{Mo}^{++++++}$
Hydrazoic acid (3)	$2\mathrm{HN_3} \rightarrow 3\mathrm{N_2} + 2\mathrm{H}^+$	Nitrite (1) (3)	$\mathrm{NO_2} \xrightarrow{-} \mathrm{NO_3}^{-}$
Hydrogen peroxide (3)	$\mathrm{H_2O_2} \rightarrow \mathrm{O_2} + 2\mathrm{H}^+$	Oxalate (1) (3)	$\mathrm{C_2O_4} \xrightarrow{--} 2\,\mathrm{CO_2}$
Hydroquinone (2) (3)	$\mathrm{C_6H_4O_2H_2} \rightarrow \mathrm{C_6H_4O_2} + 2\,\mathrm{H}^+$	Tellurium (3)	$\mathrm{TeO_3} \xrightarrow{--} \mathrm{TeO_4}^{--}$
Iodide (1) (3)	$2\,\mathrm{I}^- \rightarrow \mathrm{I_2}$	Thallium (3)	$\mathrm{Tl} \xrightarrow{+} \mathrm{Tl}^{+++}$
Iron (1) (2) (3)	$\mathrm{Fe} \xrightarrow{++} \mathrm{Fe}^{+++}$	Tin (1) (2) (3)	$\mathrm{Sn} \xrightarrow{++} \mathrm{Sn}^{++++}$
Lead (1)	$\mathrm{PbO_2} \rightarrow \mathrm{PbO}$	Titanium (1) (2) (3)	$\mathrm{Ti} \xrightarrow{+++} \mathrm{Ti}^{++++}$
Manganese (neutral solution) (1)	$\mathrm{Mn} \xrightarrow{++} \mathrm{Mn}^{++++}$	Uranium (1) (3)	$\mathrm{U} \xrightarrow{++++} \mathrm{UO_2}^{++}$
		Vanadium (1)	$\mathrm{V} \xrightarrow{++} \mathrm{VO_4}^{---}$
		Vanadium (1) (3)	$\mathrm{VO} \xrightarrow{++} \mathrm{VO_4}^{---}$

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* For more complete details consult N. H. Furman, Ind. Eng. Chem., Anal. Ed., 2, 213 (1930) and C. A. since 1930.

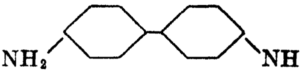
TABLE 84 — *Continued*

II. Potentiometric titrations that have been successfully made by reduction with titanous or chromous salts.

(1) = reactions with titanous solutions (2) = reactions with chromous solutions

Substance determined	Partial reaction	Substance determined	Partial reaction
Antimony (1) (2)	$\mathrm{Sb}\xrightarrow{+++++}\mathrm{Sb}^{+++}$	Molybdenum (2)	$\mathrm{Mo}\xrightarrow{++++++}\mathrm{Mo}^{+++}$
Bismuth (1)	$\mathrm{Bi}\xrightarrow{+++}\mathrm{Bi}$	Osmium (1)	$\mathrm{Os}^{+8} \rightarrow \mathrm{Os}^{+4}$ (60°C)
Bromine (1)	$\mathrm{Br}_2 \rightarrow 2\,\mathrm{Br}^-$		$\mathrm{Os}^{+4} \rightarrow \mathrm{Os}^{+3}$ (80°C)
Copper (1) (2)	$\mathrm{Cu}\xrightarrow{++}\mathrm{Cu}^{+}$	Selenium (1)	$\mathrm{SeO}_3\xrightarrow{--}\mathrm{Se}$
Ferricyanide (1)	$\mathrm{Fe(CN)}_6\xrightarrow{---}$ $\mathrm{Fe(CN)}_6^{----}$	Silver (2)	$\mathrm{Ag}\xrightarrow{+}\mathrm{Ag}$
		Thallium (1)	$\mathrm{Tl}\xrightarrow{+++}\mathrm{Tl}^{+}$
Gold (1) (2)	$\mathrm{Au}\xrightarrow{+++}\mathrm{Au}$	Tin (2)	$\mathrm{Sn}\xrightarrow{++++}\mathrm{Sn}^{++}$
Iron (1) (2)	$\mathrm{Fe}\xrightarrow{+++}\mathrm{Fe}^{++}$	Titanium (2)	$\mathrm{Ti}\xrightarrow{++++}\mathrm{Ti}^{+++}$
Mercury (1) (2)	$\mathrm{Hg}\xrightarrow{++}\mathrm{Hg}$	Uranium (1)	$\mathrm{UO}_2\xrightarrow{++}\mathrm{U}^{++++}$
Molybdenum (1)	$\mathrm{Mo}\xrightarrow{++++++}\mathrm{Mo}^{+++++}$	Vanadium (1) (2)	$\mathrm{VO}_4\xrightarrow{---}\mathrm{VO}^{++}$

III. Potentiometric titrations that have been successfully made by *precipitation with various reagents.*

Substance determined	Partial reaction	Substance determined	Partial reaction
Aluminum	$\mathrm{Al}^{+++} + 3(\mathrm{OH})^- = \mathrm{Al(OH)}_3$	Lead	(See barium and gallium)
Barium	$\mathrm{Ba}^{++} + \mathrm{CrO}_4^{--} = \mathrm{BaCrO}_4$ (Similar reactions for Hg^+ and Pb^{++})	Magnesium	$\mathrm{Mg}^{++} + 2\,\mathrm{OH}^{--} = \mathrm{Mg(OH)}_2$
Copper	$\mathrm{Cu}^+ + \mathrm{CNS}^- = \mathrm{CuCNS}$	Mercury	$\mathrm{Hg}^{++} + \mathrm{S}^{--} = \mathrm{HgS}$
Fluorine	$\mathrm{Fe}^{+++} + 6\mathrm{F}^- = \mathrm{FeF}_6^{---}$	Phosphate	$\mathrm{PO}_4^{---} + \mathrm{UO}_2^{++} + \mathrm{NH}_4^+ = (\mathrm{NH}_4)\mathrm{UO}_2\mathrm{PO}_4$
Gallium	$4\mathrm{Ga}^{+++} + 3\mathrm{Fe(CN)}_6^{----} = \mathrm{Ga}_4\,[\mathrm{Fe(CN)}_6]_3$ (Somewhat similar reactions for Cs, Ce, In, La, Rb, Pb, Ag, Th, U and Zn)	Silver or halides	$\mathrm{Ag}^+ + \mathrm{Halide}^- = \mathrm{Ag\,Halide}$ $\mathrm{Ag}^+ + \mathrm{CNS}^- = \mathrm{AgCNS}$ $\mathrm{Ag}^+ + \mathrm{K}^+ + 2\mathrm{CN}^- = \mathrm{KAg(CN)}_2$ (Somewhat similar reactions for Co, Ni, Zn)
Hydroxides	(See Hydrogen Ions by H. T. S. Britton [1929] and C. A. since 1923)		$2\mathrm{Ag}^+ + \mathrm{S}^{--} = \mathrm{Ag}_2\mathrm{S}$
Iron	$\mathrm{Fe}^{+++} + 6\mathrm{F}^- = \mathrm{FeF}_6^{---}$	Sulphate	 $+ \mathrm{H}_2\mathrm{SO}_4 = \mathrm{C}_{12}\mathrm{H}_{12}\mathrm{N}_2 \cdot \mathrm{H}_2\mathrm{SO}_4$ (Excess benzidene titrated with KNO_2)
		Thallium	$\mathrm{Tl}^+ + \mathrm{I}^- = \mathrm{TlI}$

V. ELECTROLYTIC METHODS

CHAPTER XL

ELECTROLYTIC METHODS

A. Elements That Can be Determined by Electrodeposition

In quantitative determinations by electroanalytical methods, the element is deposited on a weighed electrode which is again weighed after the electrolysis is complete. As a general rule, the element is deposited in the metallic state on the cathode, although a few elements, such as lead, are deposited as hydrated oxides on the anode. By far the greater number of electrolyses are made in solutions containing mineral acids. Some elements require special electrolytes, such as solutions containing an organic acid, an organic acid with its salt, an alkali, or a cyanide. Finally, a considerable number of elements cannot be deposited under any ordinary conditions.

The elements that can be deposited, and the types of solution that are required, are shown in Table 85. It is evident that electroanalytical methods are no more selective than the usual gravimetric or volumetric procedures, and that a given determination, as of copper in acid solution or of nickel in alkaline solution, must be preceded by separations of the elements that interfere, or else the results must be corrected for their effect.[1]

For each of the elements that can be deposited in a given electrolyte there is a definite decomposition potential, below which its ions do not give up their electrical charges and deposit on the electrode. Theoretically, therefore, it should be possible to separate any two such elements by holding the voltage constant at a pressure that lies between their decomposition potentials. Such separations have been made, but are subject to so many drawbacks that the elements are either separated before electrolysis is attempted, or the weight of the deposit is corrected for the weight of the codeposited elements as calculated from separate determinations.

B. Determination of Copper by Electrodeposition

Determinations of copper by electroanalytical methods are usually made by depositing the metal from an electrolyte containing sulphuric and nitric acids. Many types of electrodes have been recommended or used, but by

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[1] For details concerning electroanalytical methods, consult Quantitätive Analyse durch Electrolyse, by Alexander Classen, Seventh Edition, 1927, or Electro-Analysis, by E. F. Smith, Sixth Edition, 1918.

TABLE 85

Elements That Can Be Determined by Electrodeposition

(See also Table 59, page 94)

H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	$^{7}\mathrm{Cr}$	$^{8}\mathrm{Mn}$	$^{2,7}\mathrm{Fe}$	$^{3,4}\mathrm{Co}_{7,8}$	$^{3,4}\mathrm{Ni}_{7}$	$^{1,2}\mathrm{Cu}_{3,4,7}$	$^{2,3}\mathrm{Zn}_{4,7}$	$^{7?}\mathrm{Ga}$	$^{7?}\mathrm{Ge}$	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	$^{6,7}\mathrm{Mo}$	—	Ru	$^{1,7?}\mathrm{Rh}$	$^{1,3}\mathrm{Pd}_{7?}$	$^{1,3}\mathrm{Ag}_{4,7}$	$^{1,2}\mathrm{Cd}_{3,4,7}$	$^{2,4}\mathrm{In}_{7}$	$^{2,5}\mathrm{Sn}_{7}$	$^{1,5}\mathrm{Sb}$	$^{2}\mathrm{Te}$	I	Xe
Cs	Ba	La*	Hf	Ta	W	$^{1,6,7?}\mathrm{Re}$	Os	$^{7?}\mathrm{Ir}$	$^{1}\mathrm{Pt}_{7?}$	$^{1,4}\mathrm{Au}_{5,7}$	$^{1,4}\mathrm{Hg}_{5,7}$	$^{7,8}\mathrm{Tl}$	$^{1,8}\mathrm{Pb}$	$^{1,2}\mathrm{Bi}_{7}$	$^{1,7?}\mathrm{Po}_{8}$	—	Rn
—	Ra	Ac	Th	Pa	$^{6}\mathrm{U}$												

* Also elements 58–71.

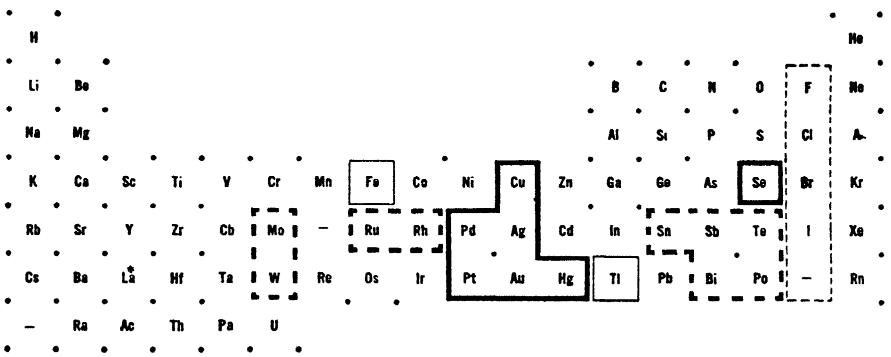
1. On cathode in mineral acid solution.
2. On cathode in organic acid solution.
3. On cathode in alkali solution.
4. On cathode in cyanide solution.
5. On cathode in alkali sulphide solution.
6. On cathode as hydrated oxide in acid solution.
7. On mercury cathode in weak acid solution. (7? denotes that deposition is complete, but apparently the method has not been described in the literature.)
8. On anode as hydrated oxide in acid solution.

far the most common and convenient are those of the cylindrical type made from sand-blasted platinum gauze. The current density employed depends on the time that can be allowed for the determination, ranging from 0.1–0.5 ampere per square decimeter in electrolyses made in still electrolytes to 1–10 amperes in rapid electrolyses in which the cathode is rotated, or the electrolyte is kept in motion by means of a stirrer, a current of air, or a magnetic field. For purposes of calculation the usual gauze electrode may be regarded as having an effective area twice that of a plain foil electrode of the same dimensions. This statement is made on the assumption that only the surface of a foil cathode next to the anode is effective in the deposition. In order to arrive at a closer approximation of the effective area of a gauze electrode, it is probably best to calculate the surface area of the wire used in making the gauze. The total length of the wire can be calculated from the number of meshes and the dimensions of the electrode. The effective area, then, will be the total length of the wire × πd where d = the diameter of the wire.

TABLE 86

Determination of Copper by Electrodeposition in a Dilute Solution of Nitric and Sulphuric Acids

(5 ml HNO_3, 5 ml H_2SO_4, 200 ml H_2O)


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo – Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po – Rn
– Ra Ac Th Pa U

* Also elements 58–71.

Heavy solid blocks inclose elements that are quantitatively deposited on the cathode.

Heavy broken blocks inclose elements that are partially deposited on the cathode.

Light solid blocks inclose elements that are not deposited, but which may retard the deposition of copper.

Light broken blocks inclose elements that are usually removed before electrodeposition is attempted.

The elements that accompany copper in determinations that are made as outlined are shown in Table 86. Of these, silver, mercury, and platinum are completely deposited on the cathode. Deposition of palladium is also complete, most of it going to the cathode, but a little being deposited, probably as hydrated oxide, on the anode. Gold present in the ionic state is completely deposited on the cathode; that present in colloidal form settles out as a sludge during the electrolysis. Gold will not remain in true solution if nitric and sulphuric are the only acids present. Small amounts of either quadri- or sexivalent selenium may remain in solution, but as a rule all of it is deposited.

Molybdenum is partially deposited from a nitric-sulphuric acid electrolyte; little, if any, is deposited from a sulphuric acid electrolyte, and contamination of copper by it can be completely avoided by solution of the deposit and redeposition. Arsenic behaves just the opposite, deposition being serious in sulphuric acid solution, and either of no consequence in the presence of nitric acid or easily overcome by redeposition if large amounts are present. Bismuth, antimony, and tellurium seriously contaminate the deposit but do not prevent complete deposition of copper. Copper tends to carry down tungsten, which must therefore be removed by digesting with acids and filtering before electrolysis is attempted. Contamination by ruthenium and rhodium is slight, but cannot be ignored. Contamination by osmium and iridium is very slight, if any, and can be avoided by redeposition. Deposition of tin is slight if it is present as stannic sulphate and the time of electrolysis is short; colloidal metastannic acid, as for example that left in solution after dissolving an alloy in nitric acid, is deposited in part. Thallium and large amounts of iron retard and may even prevent complete deposition of copper; as much as 1.0 mg of iron is without effect.

Finally, it should be mentioned in passing that two other elements, lead and manganese, do not cause any trouble at the cathode, but do deposit as hydrated dioxides on the anode. The deposition of lead can be made complete, and can serve for simultaneous determinations of copper and moderate amounts of lead. Manganese, on the other hand, cannot be completely deposited under ordinary conditions.

VI. COLORIMETRIC METHODS

CHAPTER XLI

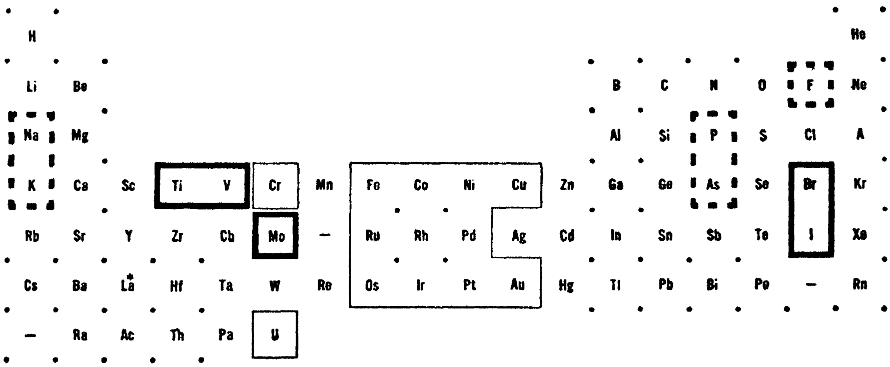
COLORIMETRIC METHODS

A. Elements That Yield Soluble Colored Compounds with Hydrogen Peroxide in Acid Solutions

The peroxide method, which is almost universally used for the determination of small amounts of titanium, is based on the yellow to amber-colored compound which titanium forms when a sulphuric acid solution of its sulphate is treated with hydrogen peroxide. The determination is usually made by adding a moderate excess of peroxide to a diluted sulphuric acid solution (1 + 20) of titanium sulphate, and then matching the color against a measured portion of a standard solution of titanium sulphate which has been treated in similar fashion.

TABLE 87

Colorimetric Determination of Titanium by the Peroxide Method


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U

* Also elements 58–71. (See text.)

Heavy solid blocks inclose elements that give colored compounds with hydrogen peroxide in dilute sulphuric acid.

Heavy broken blocks inclose elements whose compounds bleach the color of the titanium compound.

Light solid blocks inclose elements that form colored compounds that do not change color on addition of hydrogen peroxide.

Elements that interfere in such determinations are shown in Table 87. Of these, fluorine, arsenic, and phosphorus (as hydrofluoric, arsenic, or phosphoric acids) and the alkalies (as sulphates) bleach the colored titanium compound. The bleaching action of fluorine is so serious that it must be entirely removed. In fact, the bleaching effect of fluorine is the basis of a colorimetric method for its determination. The action of moderate amounts of the others is relatively slight, and can be compensated by adding like amounts to the comparison solution. If they are present in large amounts, they must be removed, as by precipitating the titanium with sodium hydroxide, filtering, and dissolving the precipitate in sulphuric acid before making the test.

In another class are vanadium, molybdenum, bromine, and iodine, which also yield colored compounds with hydrogen peroxide, the colors being reddish-brown, yellow, yellow, and yellow to reddish-brown, respectively. These elements must therefore be removed before the determination of titanium is attempted. It is interesting to note that the color of titanium can be entirely destroyed by adding hydrofluoric acid, but the color of vanadium is not affected.

Finally, the test for titanium cannot be applied in the presence of large amounts of colored sulphates such as those of iron, chromium, cobalt, nickel, copper, gold, uranium, certain rare earths, and the platinum metals. The effect of small amounts can be compensated by matching the colors of the unknown and the comparison solution before peroxide is added.

B. Elements That Yield Soluble Colored Compounds with Hydrogen Peroxide in Alkaline Solutions

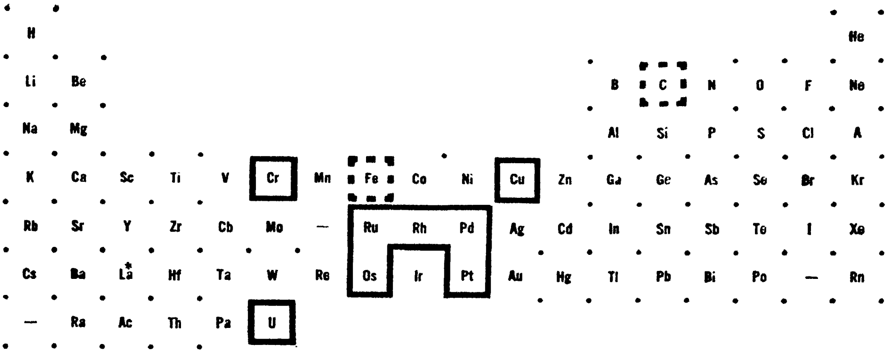
Small amounts of chromium are often determined by colorimetric comparison with standards after oxidation to the sexivalent (chromate) stage. Such oxidations are usually made in hot solutions containing approximately 5 g of sodium hydroxide and 1 g of sodium peroxide, or equivalent of hydrogen peroxide, per 100 ml. Any precipitate that may form (hydrated oxides of iron, nickel, cobalt, etc.) is removed by filtration, and the yellow color of the chromate in the filtrate is compared with the color of a standard solution of sodium chromate or of trivalent chromium which has been similarly treated. The elements yielding colored solutions under such conditions are shown in Table 88.

Of these, copper yields a blue color because its precipitate is slightly soluble in a 5 per cent solution of sodium hydroxide. Carbon yields a yellow color if decomposition of organic matter (as for example by attack with nitric and sulphuric acids) has been incomplete, or if solutions of the alkalies are filtered through paper that has not first been treated with alkali. The other indicated elements also give yellowish colors resembling that given by chromium. Occasionally a colloidal compound of iron passes through the filter and imparts a brownish-yellow color to the solution. Trouble from this source is indicated if a brownish colored compound separates from the solution after it has stood for several hours. The colors imparted by osmium, ruthenium, and palladium can be destroyed by adding ammonium chloride to the cooled sodium hydroxide solution.

Titanium, vanadium, bromides, iodides, and, under some conditions, chlorides yield colors if treated with peroxide in *acid* solution, but such solutions immediately become colorless when rendered alkaline. Gold and mercury are reduced to the metallic state.

TABLE 88

Elements That Form Colored Compounds in Dilute Solutions of Sodium Hydroxide Containing Peroxide

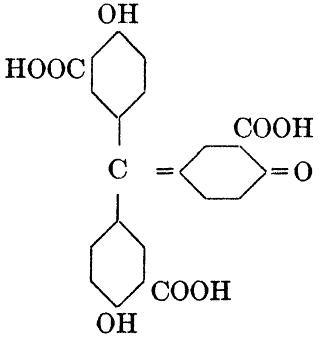


H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

* Also elements 58–71.
Solid blocks inclose elements that yield colored solutions.
Broken blocks inclose elements that may yield colored solutions under certain conditions.

C. Colorimetric Determination of Aluminum by the Formation of a Lake with Aurintricarboxylic Acid

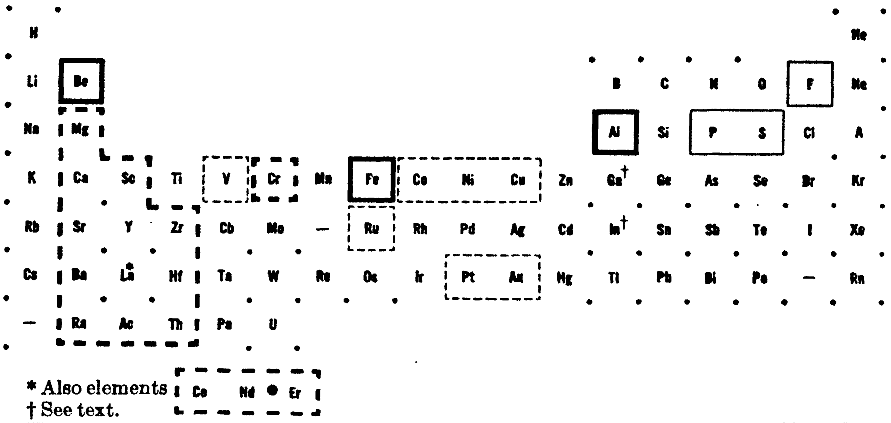
Colorimetric determinations of aluminum by the use of aurintricarboxylic acid



are confined to minute amounts of aluminum, not above 0.1 mg per 100 ml of solution. The test is ordinarily made by (1) obtaining the aluminum in 75 ml of a clear solution that contains 5 ml of hydrochloric acid, and is free from interfering elements; (2) treating with 5 ml of a 0.2 per cent solution of the ammonium salt of aurintricarboxylic acid, and then with 5 ml of glacial acetic acid; (3) adding ammonium hydroxide, slowly and with stirring, until the solution is alkaline to litmus; (4) adding 5 ml of glacial acetic acid; (5) allowing the solution to stand for 15 minutes; (6) again rendering the solution alkaline; and (7) adding 5 ml of ammonium hydroxide in excess. Ammonium carbonate is substituted for ammonium hydroxide if alkaline earths, magnesium, rare earths, zirconium, hafnium, thorium, chromium, or gallium are present. The color developed is compared with that obtained with suitable portions of a standard solution carried through the same procedure.

TABLE 89

Colorimetric Determination of Aluminum by the Formation of a Lake with Aurintricarboxylic Acid


H He
Li Be B C N O F Ne
Na Mg Al Si P S Cl A
K Ca Sc Ti V Cr Mn Fe Co Ni Cu Zn Ga† Ge As Se Br Kr
Rb Sr Y Zr Cb Mo — Ru Rh Pd Ag Cd In† Sn Sb Te I Xe
Cs Ba La* Hf Ta W Re Os Ir Pt Au Hg Tl Pb Bi Po — Rn
— Ra Ac Th Pa U
Ce Nd Er

* Also elements Ce Nd Er

† See text.

Heavy solid blocks inclose elements that form colored lakes in the presence of NH_4OH or $(NH_4)_2CO_3$.

Heavy broken blocks inclose elements that form colored lakes in the presence of NH_4OH but not of $(NH_4)_2CO_3$.

Light solid blocks inclose elements that have a bleaching effect on the color of the aluminum lake.

Light broken blocks inclose elements that interfere because they form colored solutions or precipitates.

In this method the first consideration is to obtain a satisfactory grade of the aurin compound; to be of service it should give, when carried through the process, a barely perceptible straw-yellow color in a final volume of 100 ml of a solution containing no aluminum, and a clear pink color in a solution containing 0.005 mg of aluminum. The second consideration is to avoid the introduction of aluminum through reagents or attack on glassware.

The elements that cause difficulties in the test are shown in Table 89.

Of these, beryllium and iron give red and wine-red colored lakes, respectively, and must be removed before the test is made. Magnesium interferes to a greater extent than the alkaline earths. The effect of magnesium in low concentrations, the alkaline earths in moderate concentrations, and elements such as the rare earths, zirconium, hafnium, thorium, and chromium can be avoided by substituting ammonium carbonate for ammonium hydroxide. In either reagent gallium gives a lake which resembles that of aluminum only when it is present in such extreme dilutions as 0.001 mg per 100 ml. With higher concentrations, as for example 20 mg, the color of the lake is light brownish orange and does not seriously disturb the detection or determination of moderate amounts, such as 0.05 mg, of aluminum. The lake formed by indium is orange-pink, but so feeble that as much as 10 mg causes no difficulties. Phosphorus in high concentrations, sulphur in the form of hydrogen sulphide or sulphur dioxide, and particularly fluorine, bleach the color of the aluminum lake.

Of the elements that interfere because they form colored solutions or precipitates, ruthenium yields a colored solution, platinum yields the yellow colored chloroplatinate, and gold is reduced to the elemental state. Such amounts of the last two as may remain in solution do not interfere. Rhodium, osmium, and iridium yield colored solutions but do not interfere seriously when present in moderate concentrations, such as 10 mg per 100 ml. Vanadium in the quinquevalent state imparts a yellow color to the solution if more than a milligram or so is present; in the quadrivalent state it tends to intensify the color of the aluminum lake and even to give a more or less fugitive color with the dye alone.

VII. SPECTROCHEMICAL METHODS

CHAPTER XLII

SPECTROCHEMICAL METHODS

The application of the spectroscope to the qualitative and quantitative analysis of materials is steadily increasing as the methods are perfected and new uses made evident. In the past, spectroscopic methods were applied qualitatively as a test of purity or in the identification of small or valuable samples; present-day methods find increased application not only in qualitative tests but also in the quantitative analysis of many materials.

Qualitative spectrochemical analysis, because of rapidity and certainty under properly controlled conditions, is invaluable in the examination of samples preliminary to chemical determinations. The test may be applied to widely differing classes of materials including metals, alloys, precipitates, salts, refractories, glass, minerals, soils, and rocks. Tests for certain elements such as strontium in calcium oxide or rubidium in alkali chlorides obtained in the analysis of rocks can be made quite satisfactorily by visual examination of emission spectra. More certain results and, at the same time, permanent records of the tests are obtained in photographed spectra.

Photography of the ultra-violet and blue region of the spectrum suffices for most analytical work, although the range between the shorter ultraviolet and the infra-red (2000 to 10,000 A) may be covered with the usual technique and instruments if necessary. The sensitivity of the test in this range varies with the type of material under analysis, the procedure used, and the element for which the test is made. Under comparable conditions, the elements exhibit differences in sensitivity depending mainly on the constitution of the atom. In Table 90 the outstanding differences in the sensitivity of the elements are shown. For the elements generally classed as insensitive, the gases, halogens, and some metalloids, a fair sensitivity may be realized by photography in the ultra-violet below 2000 A, necessitating the use of spectrographs designed to permit evacuation. Little application has been made of this region of the spectrum in analytical work.

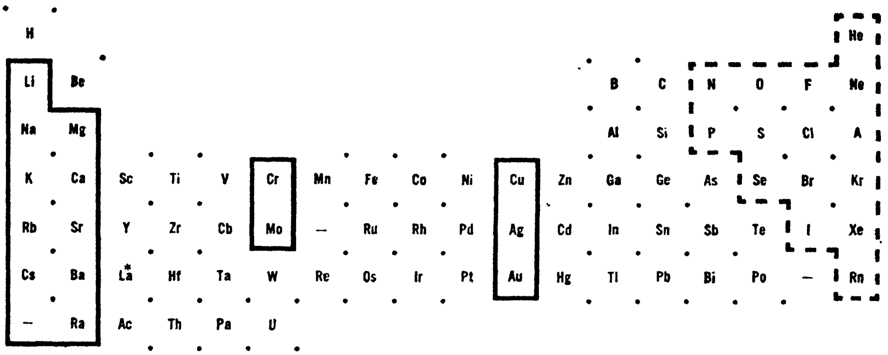
Quantitative spectrochemical analysis has been applied most fruitfully in the routine determination of minor constituents in metals and alloys, in the study of the distribution of trace elements in biochemical and agricultural investigations, and in the analysis of rocks and minerals. The principles which underlie quantitative spectrochemical methods have been well established during the past few years, and refined methods are rapidly becoming available. Semi-quantitative tests in which the concentration of the element may be given to a factor of 10, i.e., a distinction in percentages between thousandths, hundredths, tenths, or greater than tenths, can be made with little difficulty after the analyst has become experienced.

More accurate results can be obtained by the comparison of the intensities of the spectral lines of the element in the unknown sample with the intensities in the spectra of a series of samples having known compositions as determined either by careful chemical analysis or by synthesis. In analyses where the source of excitation has been controlled for optimum conditions and the line intensities have been compared by refined methods, the accuracy has been increased to values ranging from ±10 per cent to ±2 per cent of the concentration of the element determined. Thus, from the standpoint of accuracy, the spectrochemical method is seen to compete with the chemical in the range of concentrations below 10 per cent. The increase in speed and, in certain cases, reliability of test, combined with the attainment of comparable accuracy, has enabled an economical substitution of spectrochemical methods for chemical in the routine analysis of such metals as zinc, nickel, and magnesium alloys, despite the rather high cost of equipment.

TABLE 90

Sensitivity of Spectrochemical Tests for the Elements

(In wave-length range 2000–10,000 Ångström units)



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	—	Rn
—	Ra	Ac	Th	Pa	U												

* Also elements 58–71.

Heavy solid blocks inclose elements for which test is of high sensitivity (of the order of 1 part in 1,000,000).

Heavy broken blocks inclose elements for which test is insensitive. For the detection or determination of small percentages of these, special procedures are usually required.

Elements not inclosed in blocks are those for which test is of average sensitivity (on the order of 1 part in 100,000). Of these, elements adjacent to elements of high sensitivity are somewhat more sensitive than the average, while those adjacent to the insensitive elements are somewhat less sensitive than the average.

The apparatus for this work consists of a spectrograph, a source for the excitation of the spectrum of the sample under test, and a device for the examination of the photographed spectrum for identification of lines and comparison of intensities. The quartz prism spectrograph is generally employed although the grating spectrograph may be used to an increasing extent in the future. The choice of a spectrograph depends on the type of analysis for which it is to be used, the requirement being that the line images in the spectrum be sufficiently well defined and separated from one another for study. For simpler spectra, such as those for the common non-ferrous metals, smaller and less costly instruments may be employed, but for general work, the larger types are necessary.

The excitation sources used at the present time are the electrical arc or spark, the gas flame being applied only to a limited extent.

The instruments for examination of the photographed spectra for comparison of intensities vary considerably in design, the simpler types consisting merely of an illuminated viewing box and a hand lens. The simple type may be supplemented by a densitometer with which refined intensity comparisons may be made by means of a photoelectric cell and galvanometer.

The instruments required are available commercially and are described in manufacturers' catalogues as well as in the literature on spectrochemical analysis.

PART IV. DIAGRAMMATIC OUTLINES OF METHODS OF ANALYSIS

The following diagrams of methods of chemical analysis are presented because they give clearer pictures of what goes on in the course of the analyses than can be obtained from descriptions of the methods. The diagrams cover analyses in the fields of rocks, limestones, and ceramic materials, and of ferrous and non-ferrous metals. They have been chosen to illustrate the applications of gravimetric, volumetric, potentiometric, colorimetric, and electrolytic methods of analysis, and embrace simple determinations, more or less complex analyses, difficulties that may be caused by the presence of certain elements, modifications that must be made to meet changed conditions, and precautions that must be taken in umpire versus routine analyses.

The compositions shown under the materials represent typical specimens, and do not necessarily include all the constituents that may be found in the materials.

CHAPTER XLIII

ANALYSIS OF LIMESTONE

($CaCO_3$ CONTAINING MORE OR LESS $MgCO_3$, SiO_2, Al_2O_3, AND Fe_2O_3)

A. Determination of CO_2

In this determination, the limestone is dissolved in diluted hydrochloric acid, the resulting gases and vapors are forced through reagents that absorb everything but air and carbon dioxide, and the latter is then absorbed in a vessel which is weighed before and after the absorption takes place.

The steps of the process are illustrated in Table 91.

NOTES

[1] Hydrogen sulphide or chlorine, which might be present at this point if the sample contained a soluble sulphide or manganese dioxide, will also be removed by the copper sulphate.

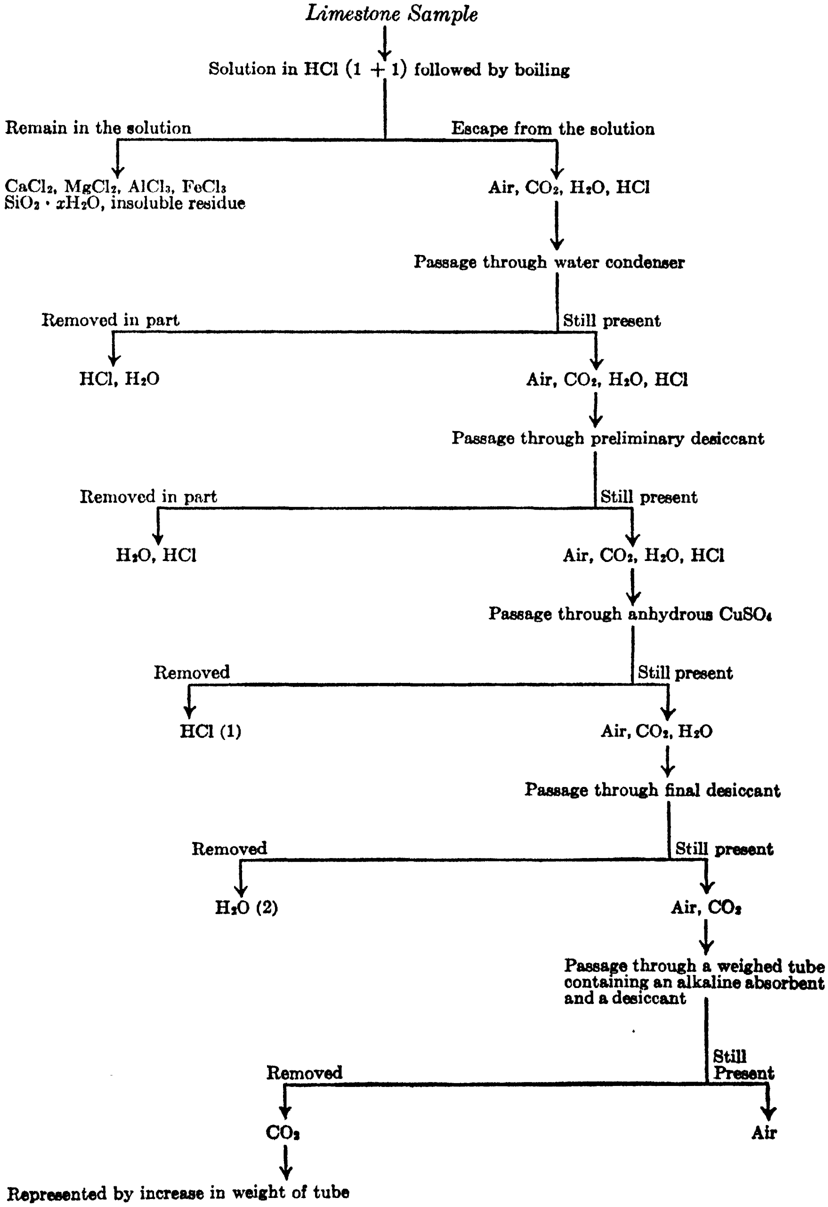
[2] Water is removed from the gas stream at four points as follows: (1) the condenser removes water that would otherwise overburden the preliminary desiccant; (2) the preliminary desiccant must be of greater drying power than anhydrous copper sulphate, which would otherwise become hydrated and lose its power to absorb hydrochloric acid; (3) the " final " desiccant is used to make sure that the gases are dry *before* they enter the weighed tube; and (4) the " final " desiccant is also placed in the exit end of the weighed tube to absorb the water liberated in the reaction between carbon dioxide and the alkaline absorbent.

TABLE 91

Analysis of Limestone

$CaCO_3$ containing more or less $MgCO_3$, Al_2O_3, Fe_2O_3, and SiO_2

A. Determination of CO_2


Limestone Sample
Solution in HCl (1 + 1) followed by boiling
Remain in the solution
Escape from the solution
CaCl₂, MgCl₂, AlCl₃, FeCl₃
SiO₂ · xH₂O, insoluble residue
Air, CO₂, H₂O, HCl
Passage through water condenser
Removed in part
Still present
HCl, H₂O
Air, CO₂, H₂O, HCl
Passage through preliminary desiccant
Removed in part
Still present
H₂O, HCl
Air, CO₂, H₂O, HCl
Passage through anhydrous CuSO₄
Removed
Still present
HCl (1)
Air, CO₂, H₂O
Passage through final desiccant
Removed
Still present
H₂O (2)
Air, CO₂
Passage through a weighed tube containing an alkaline absorbent and a desiccant
Removed
Still Present
CO₂
Air
Represented by increase in weight of tube

B. Determinations of SiO_2, Fe_2O_3, Al_2O_3, CaO, and MgO.

If very little material is available, these determinations can be made in the hydrochloric acid solution left after the determination of carbon dioxide as in *A*. Otherwise a new sample is taken, and the analysis is made as described under the General Procedure (page 30). The steps of the process are illustrated in Table 92.

NOTES

[1] This does not represent all the SiO_2 in the sample. A small amount, usually not more than 1 mg, remains in solution after the double evaporations with hydrochloric acid, and may be recovered by appropriate treatments of the $Fe_2O_3 + Al_2O_3$ residue if very accurate results are desired (see Note 4).

[2] It is important that the weight of the impurities be small (not above 1–2 mg) and that it does not change as a result of the treatments between weighings.

[3] If the material contains members of the hydrogen sulphide group, these are separated at this point by adjusting the acidity, treating with hydrogen sulphide, and filtering. The precipitate is then dissolved and tested for its components, while the filtrate is boiled to expel hydrogen sulphide, treated with nitric acid to reoxidize the iron, and neutralized with ammonium hydroxide as outlined. The filtrate left after the separation of silica must also be treated with an oxidant if the solution was evaporated in platinum.

[4] The ignited precipitate always contains more or less of the silica that was lost in (1). In addition it will contain all of any P_2O_5, TiO_2, ZrO_2, or other members of the Ammonium Hydroxide Group (page 56) that may be present in the limestone. The retention of V_2O_5 is also quite complete, although this depends on the kind and amount of the members of the ammonium hydroxide group that are present. For the colorimetric determination of titanium in this precipitate see page 171, and for the determination of zirconium see page 92.

[5] Elements such as titanium or vanadium also react with zinc in sulphuric acid solution to form compounds that consume potassium permanganate. When present in the limestone, they cause high values for iron oxide.

[6] The weight of Al_2O_3 will be too high if the limestone contains P_2O_5 or ZrO_2 and their weights are not determined and deducted. The effects of TiO_2 and V_2O_5 depend on the method of determining Fe_2O_3. If iron is reduced by zinc and titrated with permanganate it so happens that equal weights of TiO_2 and Fe_2O_3 require exactly the same amount of potassium permanganate, and so all the TiO_2 is counted as Fe_2O_3 and none of it as Al_2O_3. Under the same circumstances a given weight of V_2O_5 requires more permanganate than the same weight of Fe_2O_3; consequently, in addition to increasing the apparent amount of Fe_2O_3, it decreases the apparent amount of Al_2O_3.

[7] If the limestone contains manganese, all of it should be caught in this filtrate. Its interference in the subsequent steps of the analysis can be avoided by removing it at this point, as, for example, by precipitating with pure ammonium sulphide and filtering.

[8] This does not represent all the CaO in the sample, for the precipitation of calcium as oxalate is never complete. The small amount left in solution (usually not over 0.5 mg) will be found in the $Mg_2P_2O_7$ (see 9, below) and must be recovered in analyses of the highest accuracy. Strontium, if it is present in the limestone, will be caught with the CaO and weighed, as SrO, at this point. Manganese, if it has not been removed, will be caught in small part and weighed as Mn_3O_4.

[9] The $Mg_2P_2O_7$ obtained at this point contains any calcium, chiefly as $Ca_3(PO_4)_2$, which escaped precipitation as the oxalate. All manganese that has not been removed will also be contained in the precipitate as $Mn_2P_2O_7$. Barium will also be present in part, chiefly as $Ba_3(PO_4)_2$, if it is a constituent of the limestone.

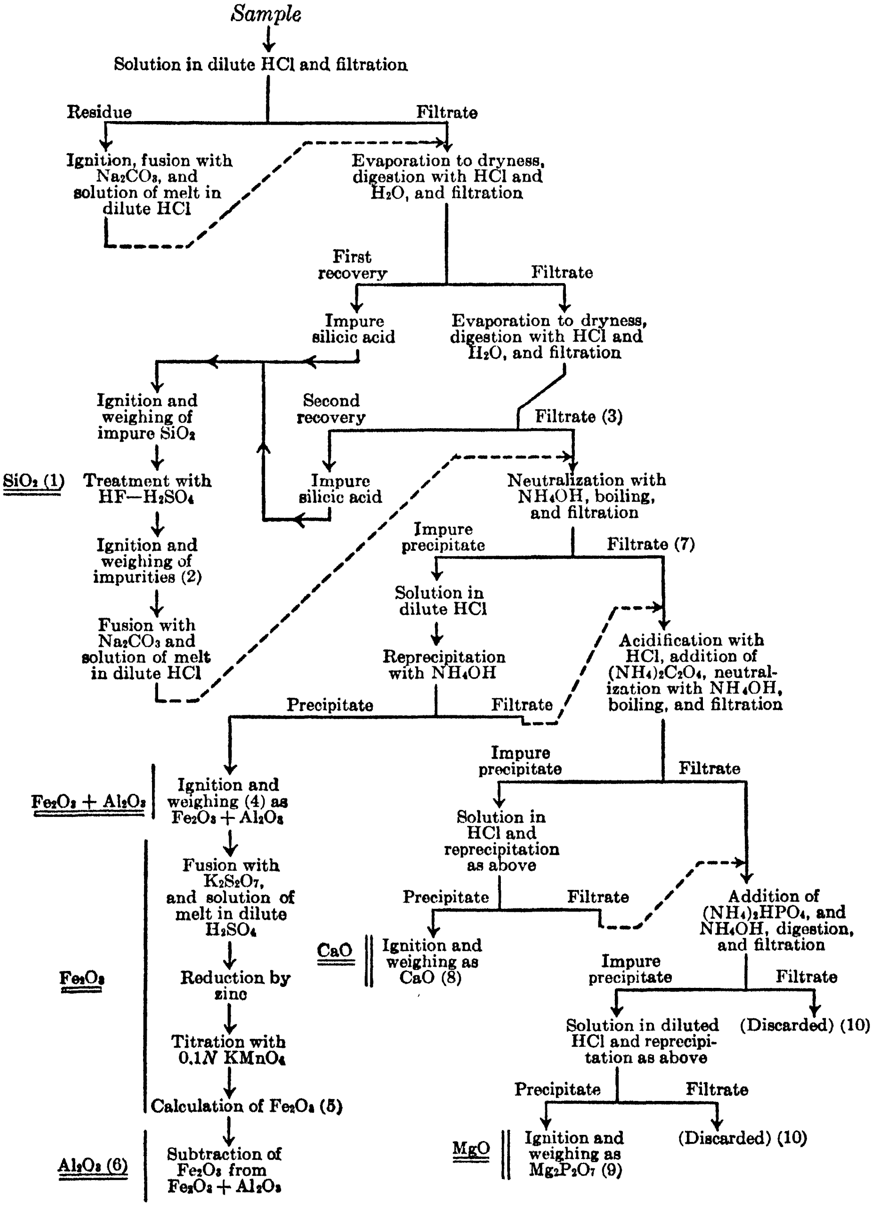
[10] The discarded filtrates contain any alkalies that may have been present in the sample, but cannot be used for their determination because sodium carbonate was introduced at the start of the analysis, and phosphate was added in the determination of magnesium. The alkalies are, therefore, determined in a separate sample by the J. Lawrence Smith method (page 75).

The only modification of the method that is needed in analyses of silicate rocks is to fuse the whole sample with sodium carbonate instead of first treating it with acid.

TABLE 92

Analysis of Limestone (*continued*)

B. Determination of SiO_2, Fe_2O_3, Al_2O_3, CaO, and MgO


Sample
Solution in dilute HCl and filtration
Residue
Filtrate
Ignition, fusion with Na_2CO_3, and solution of melt in dilute HCl
Evaporation to dryness, digestion with HCl and H_2O, and filtration
First recovery
Filtrate
Impure silicic acid
Evaporation to dryness, digestion with HCl and H_2O, and filtration
Ignition and weighing of impure SiO_2
Second recovery
Filtrate (3)
SiO_2 (1)
Treatment with HF—H_2SO_4
Impure silicic acid
Neutralization with NH_4OH, boiling, and filtration
Impure precipitate
Filtrate (7)
Ignition and weighing of impurities (2)
Solution in dilute HCl
Fusion with Na_2CO_3 and solution of melt in dilute HCl
Reprecipitation with NH_4OH
Acidification with HCl, addition of $(NH_4)_2C_2O_4$, neutralization with NH_4OH, boiling, and filtration
Precipitate
Filtrate
Impure precipitate
Filtrate
$Fe_2O_3 + Al_2O_3$
Ignition and weighing (4) as $Fe_2O_3 + Al_2O_3$
Solution in HCl and reprecipitation as above
Fusion with $K_2S_2O_7$, and solution of melt in dilute H_2SO_4
Precipitate
Filtrate
Addition of $(NH_4)_2HPO_4$, and NH_4OH, digestion, and filtration
CaO
Ignition and weighing as CaO (8)
Fe_2O_3
Reduction by zinc
Impure precipitate
Filtrate
Solution in diluted HCl and reprecipitation as above
(Discarded) (10)
Titration with 0.1*N* $KMnO_4$
Precipitate
Filtrate
Calculation of Fe_2O_3 (5)
MgO
Ignition and weighing as $Mg_2P_2O_7$ (9)
(Discarded) (10)
Al_2O_3 (6)
Subtraction of Fe_2O_3 from $Fe_2O_3 + Al_2O_3$

CHAPTER XLIV

DETERMINATION OF ALKALIES IN FELDSPAR

In the J. Lawrence Smith method, which is described on page 75, the alkalies are converted to soluble chlorides by fusing the feldspar with ammonium chloride and calcium carbonate, and weighed as such after they have been freed from accompanying elements. Potassium is next precipitated and weighed as the chloroplatinate. If, as is usual, sodium and potassium are the only alkalies present, simple calculations then serve to establish their amounts. The steps of the process are illustrated in Table 93.

NOTES

[1] As a rule the insoluble residue retains little, if any, sodium or potassium. In analyses of the highest accuracy, it is ignited and again carried through the treatment, and the water extracts are combined.

[2] If the sulphate ion is present, it must be removed as barium sulphate at this point by treating with barium chloride and filtering. The excess of barium is then removed by treating the filtrate with ammonium carbonate and again filtering.

[3] Ignition of the alkali chlorides in the presence of ammonium oxalate always gives rise to some alkali carbonate, which must be converted to chlorides before weighing.

[4] Residues obtained at this point are composed chiefly of silica and should not weigh more than a few tenths of a milligram in careful work.

[5] Rubidium and cesium, which are rarely encountered, would quantitatively accompany potassium as chloroplatinates.

[6] A direct determination of sodium oxide can be made by treating the filtrate with hydrogen, filtering to remove the platinum, evaporating, igniting, weighing the sodium chloride, and calculating to the oxide. As a general rule, the weight of sodium oxide is calculated after subtracting the KCl equivalent of the K_2PtCl_6 or K_2O from the weight of NaCl + KCl. Lithium, which is seldom encountered, accompanies sodium throughout the analysis, although some of it is lost in the residue left at the start, and in the calcium carbonate and calcium oxalate precipitates. The probable effects of other elements are discussed on pages 75 to 77.

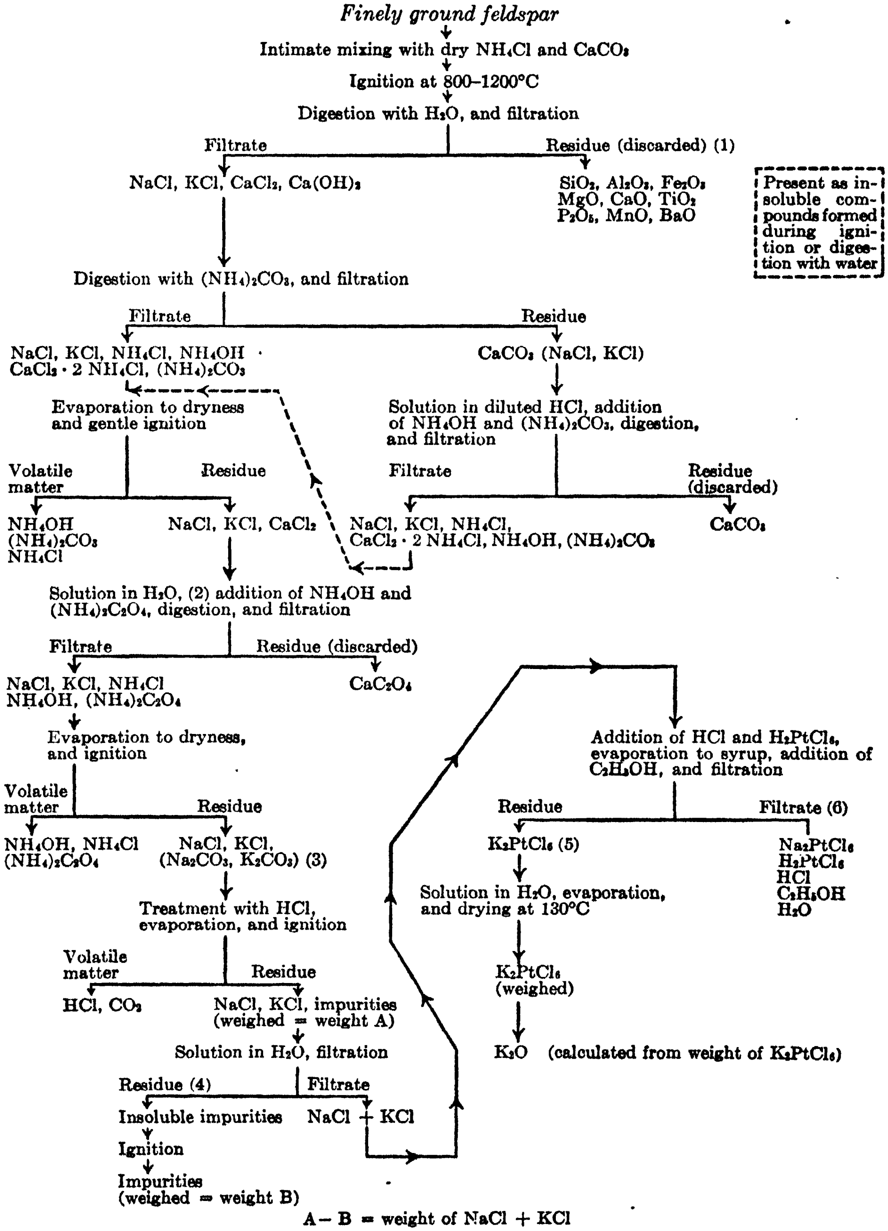
The method as outlined serves for the determination of alkalies in materials such as rocks, clays, soda-lime glass, and, with suitable modifications, for limestones and special glasses (see Table 48, page 76).

TABLE 93

Analysis of Feldspar

(SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, BaO, Na_2O, K_2O, TiO_2, P_2O_5, MnO)

Determination of Alkalies


Finely ground feldspar
Intimate mixing with dry NH_4Cl and $CaCO_3$
Ignition at 800–1200°C
Digestion with H_2O, and filtration
Filtrate
Residue (discarded) (1)
$NaCl$, KCl, $CaCl_2$, $Ca(OH)_2$
SiO_2, Al_2O_3, Fe_2O_3, MgO, CaO, TiO_2, P_2O_5, MnO, BaO
Present as insoluble compounds formed during ignition or digestion with water
Digestion with $(NH_4)_2CO_3$, and filtration
Filtrate
Residue
$NaCl$, KCl, NH_4Cl, NH_4OH, $CaCl_2 \cdot 2\,NH_4Cl$, $(NH_4)_2CO_3$
$CaCO_3$ ($NaCl$, KCl)
Evaporation to dryness and gentle ignition
Solution in diluted HCl, addition of NH_4OH and $(NH_4)_2CO_3$, digestion, and filtration
Volatile matter
Residue
Filtrate
Residue (discarded)
NH_4OH, $(NH_4)_2CO_3$, NH_4Cl
$NaCl$, KCl, $CaCl_2$
$NaCl$, KCl, NH_4Cl, $CaCl_2 \cdot 2\,NH_4Cl$, NH_4OH, $(NH_4)_2CO_3$
$CaCO_3$
Solution in H_2O, (2) addition of NH_4OH and $(NH_4)_2C_2O_4$, digestion, and filtration
Filtrate
Residue (discarded)
$NaCl$, KCl, NH_4Cl, NH_4OH, $(NH_4)_2C_2O_4$
CaC_2O_4
Evaporation to dryness, and ignition
Volatile matter
Residue
NH_4OH, NH_4Cl, $(NH_4)_2C_2O_4$
$NaCl$, KCl, (Na_2CO_3, K_2CO_3) (3)
Treatment with HCl, evaporation, and ignition
Volatile matter
Residue
HCl, CO_2
$NaCl$, KCl, impurities (weighed = weight A)
Solution in H_2O, filtration
Residue (4)
Filtrate
Insoluble impurities
$NaCl + KCl$
Ignition
Impurities (weighed = weight B)
A − B = weight of $NaCl + KCl$
Addition of HCl and H_2PtCl_6, evaporation to syrup, addition of C_2H_5OH, and filtration
Residue
Filtrate (6)
K_2PtCl_6 (5)
Na_2PtCl_6, H_2PtCl_6, HCl, C_2H_5OH, H_2O
Solution in H_2O, evaporation, and drying at 130°C
K_2PtCl_6 (weighed)
K_2O (calculated from weight of K_2PtCl_6)

CHAPTER XLV

ROUTINE DETERMINATION OF Al_2O_3 IN BAUXITE

The following procedure for the determination of alumina in bauxite illustrates the difficulties that attend a reasonably rapid gravimetric determination of a constituent that does not enter into a selective reaction by which it can be separated from the constituents that accompany it. In this method the sample is decomposed by treating with nitric, hydrofluoric, and sulphuric acids. All silicon and hydrofluoric acid are then expelled by evaporating to fumes of sulphuric acid. If an insoluble residue remains, it is separated and fused with sodium carbonate, and the melt is dissolved and added to the main solution. This is then diluted to a definite volume and thoroughly mixed, and three aliquot portions are withdrawn. One of these is treated with ammonium hydroxide and filtered, and the precipitate is ignited and weighed to obtain the weight of the oxides of the constituents of bauxite that are precipitated by ammonium hydroxide. The second portion is made quite acid (1 + 9), treated with cupferron, and filtered, and the precipitate is ignited and weighed to obtain the weight of the oxides of the constituents of bauxite that are precipitated by cupferron. The third portion is used for the determination of P_2O_5 by the customary precipitation as ammonium phosphomolybdate, followed by conversion to magnesium ammonium phosphate and ignition to magnesium pyrophosphate. The difference between the weight of the oxides obtained from the first portion, and the sum of the weights of the oxides obtained from the second and third portions, represents the weight of aluminum oxide. This weight will be in error if the bauxite contains elements besides aluminum and phosphorus that are precipitated by ammonium hydroxide, and not by cupferron. As a rule such elements occur in very small amount if at all, and their effect can be disregarded in routine analyses. The steps of the process are illustrated in Table 94.

NOTES

[1] These are the constituents that are present in the National Bureau of Standards Standard Sample of Bauxite No. 69.

[2] This solution must be free from silicic acid. If there is any doubt, the solution should be treated with hydrofluoric and sulphuric acids, evaporated to fumes of the latter, and diluted before adding to the main solution.

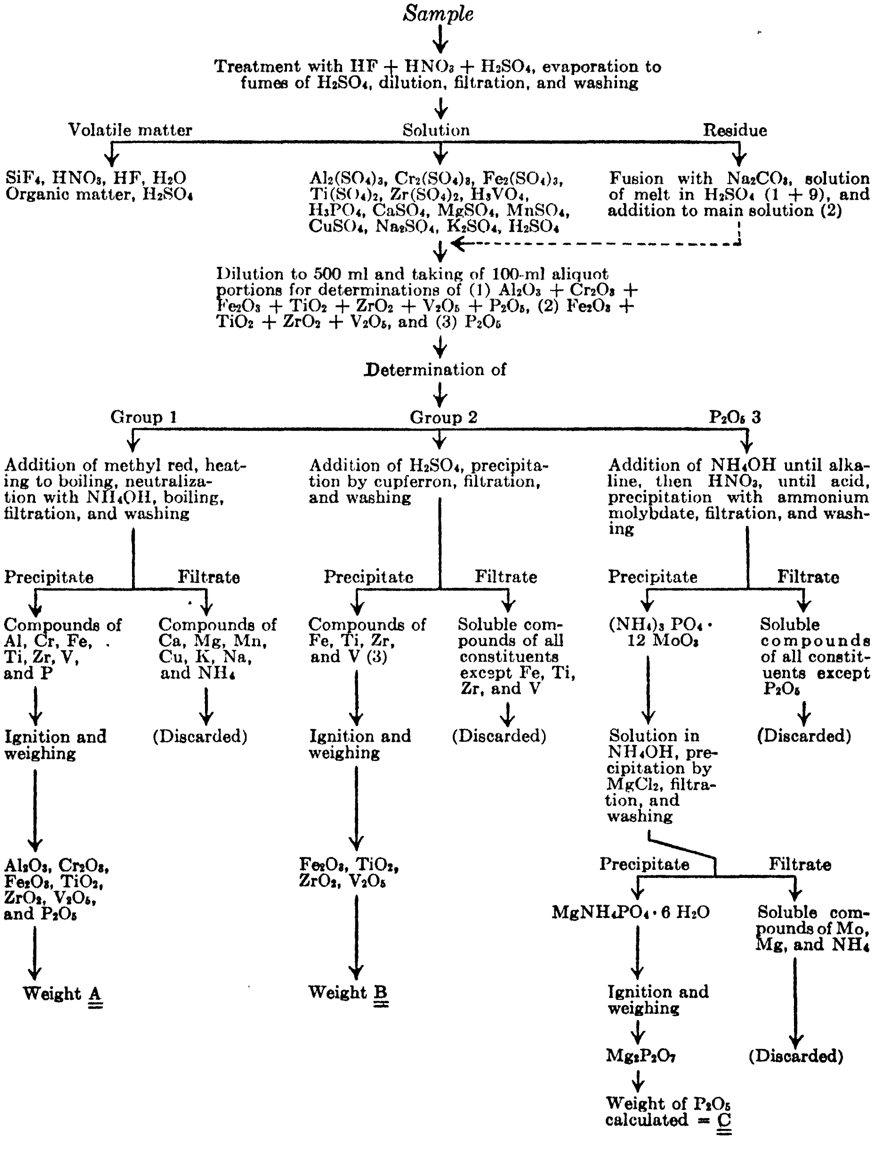
[3] Copper is very incompletely precipitated by cupferron in 10 per cent sulphuric acid solution and can be ignored in view of the small amounts present in bauxite.

[4] The amount of chromium oxide is usually so small that it can be ignored. Its amount can be determined colorimetrically by fusing with an oxidizing alkaline flux, dissolving the melt, and comparing the color of the solution with that of a standard (see Table 88, page 173).

TABLE 94

Routine Determination of Alumina in Bauxite

(Al_2O_3, Fe_2O_3, V_2O_5, Cr_2O_3, SiO_2, TiO_2, ZrO_2, P_2O_5, CaO, MgO, MnO, CuO, Na_2O, K_2O, SO_3, *volatile matter*) (1)



Sample

Treatment with HF + HNO_3 + H_2SO_4, evaporation to fumes of H_2SO_4, dilution, filtration, and washing

Volatile matter

SiF_4, HNO_3, HF, H_2O
Organic matter, H_2SO_4

Solution

$Al_2(SO_4)_3$, $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $Ti(SO_4)_2$, $Zr(SO_4)_2$, H_3VO_4, H_3PO_4, $CaSO_4$, $MgSO_4$, $MnSO_4$, $CuSO_4$, Na_2SO_4, K_2SO_4, H_2SO_4

Residue

Fusion with Na_2CO_3, solution of melt in H_2SO_4 (1 + 9), and addition to main solution (2)

Dilution to 500 ml and taking of 100-ml aliquot portions for determinations of (1) Al_2O_3 + Cr_2O_3 + Fe_2O_3 + TiO_2 + ZrO_2 + V_2O_5 + P_2O_5, (2) Fe_2O_3 + TiO_2 + ZrO_2 + V_2O_5, and (3) P_2O_5

Determination of

Group 1

Addition of methyl red, heating to boiling, neutralization with NH_4OH, boiling, filtration, and washing

Precipitate: Compounds of Al, Cr, Fe, Ti, Zr, V, and P → Ignition and weighing → Al_2O_3, Cr_2O_3, Fe_2O_3, TiO_2, ZrO_2, V_2O_5, and P_2O_5 → Weight A

Filtrate: Compounds of Ca, Mg, Mn, Cu, K, Na, and NH_4 → (Discarded)

Group 2

Addition of H_2SO_4, precipitation by cupferron, filtration, and washing

Precipitate: Compounds of Fe, Ti, Zr, and V (3) → Ignition and weighing → Fe_2O_3, TiO_2, ZrO_2, V_2O_5 → Weight B

Filtrate: Soluble compounds of all constituents except Fe, Ti, Zr, and V → (Discarded)

P_2O_5 3

Addition of NH_4OH until alkaline, then HNO_3, until acid, precipitation with ammonium molybdate, filtration, and washing

Precipitate: $(NH_4)_3PO_4 \cdot 12\,MoO_3$ → Solution in NH_4OH, precipitation by $MgCl_2$, filtration, and washing

Precipitate: $MgNH_4PO_4 \cdot 6\,H_2O$ → Ignition and weighing → $Mg_2P_2O_7$ → Weight of P_2O_5 calculated = C

Filtrate: Soluble compounds of Mo, Mg, and NH_4 → (Discarded)

Filtrate: Soluble compounds of all constituents except P_2O_5 → (Discarded)

A − [B + C] = weight of Al_2O_3 + Cr_2O_3 (4)

CHAPTER XLVI

ANALYSIS OF A WET-PROCESS ENAMEL FOR CAST IRON

The following methods illustrate changes that must be made in the General Procedure (pages 30 to 77) if the material under test contains constituents that interfere. The methods also present an interesting picture of the variety of operations that may be involved in the analysis of a single material. The material chosen for the illustration is a wet-process enamel for cast iron in which the intentional constituents are SiO_2, B_2O_3, F, PbO, BaO, Al_2O_3, CaO, K_2O, and Na_2O.

A. Determination of SiO_2

The determination of silica in this material is complicated by the presence of boron and fluorine, both of which interfere in the General Procedure (page 30). Special treatments must therefore be introduced. These differ from those in the General Procedure in that the carbonate melt is dissolved in water instead of in acid, and dehydration with acid is postponed until the silicon has been separated from fluorine and boron. The steps of the process are shown in Table 95.

NOTES

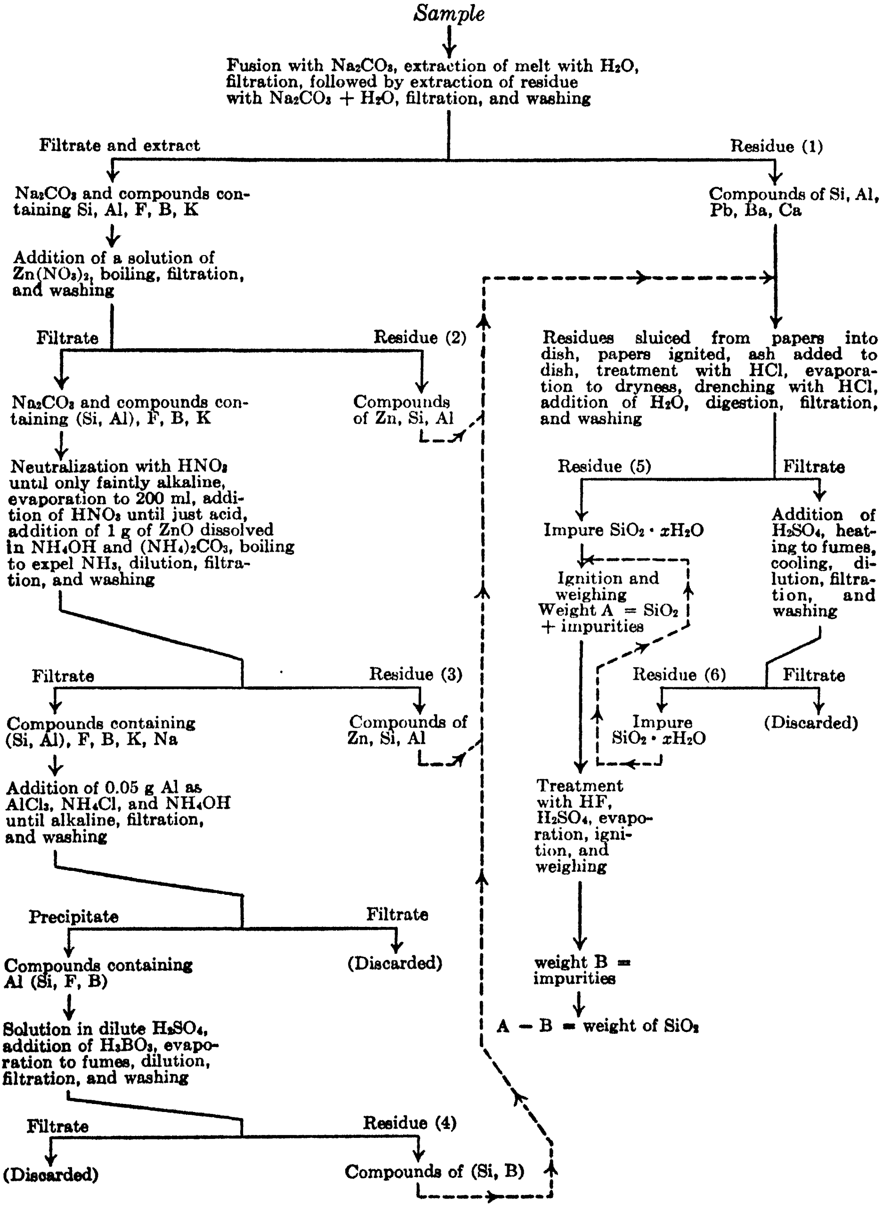
(1), (2), (3), (4), (5), (6). It will be noticed that the presence of fluorine in a siliceous material introduces so many complications in the separation of silica that residues containing silica are obtained at the six steps of the method indicated by the numbers in parentheses.

TABLE 95

Analysis of a Wet-process Enamel for Cast Iron

(SiO_2, B_2O_3, F, PbO, BaO, Al_2O_3, CaO, K_2O, Na_2O)

A. Determination of SiO_2


Sample
Fusion with Na_2CO_3, extraction of melt with H_2O, filtration, followed by extraction of residue with Na_2CO_3 + H_2O, filtration, and washing
Filtrate and extract
Residue (1)
Na_2CO_3 and compounds containing Si, Al, F, B, K
Compounds of Si, Al, Pb, Ba, Ca
Addition of a solution of $Zn(NO_3)_2$, boiling, filtration, and washing
Filtrate
Residue (2)
Na_2CO_3 and compounds containing (Si, Al), F, B, K
Compounds of Zn, Si, Al
Residues sluiced from papers into dish, papers ignited, ash added to dish, treatment with HCl, evaporation to dryness, drenching with HCl, addition of H_2O, digestion, filtration, and washing
Neutralization with HNO_3 until only faintly alkaline, evaporation to 200 ml, addition of HNO_3 until just acid, addition of 1 g of ZnO dissolved in NH_4OH and $(NH_4)_2CO_3$, boiling to expel NH_3, dilution, filtration, and washing
Residue (5)
Filtrate
Impure $SiO_2 \cdot xH_2O$
Addition of H_2SO_4, heating to fumes, cooling, dilution, filtration, and washing
Ignition and weighing
Weight A = SiO_2 + impurities
Filtrate
Residue (3)
Residue (6)
Filtrate
Compounds containing (Si, Al), F, B, K, Na
Compounds of Zn, Si, Al
Impure $SiO_2 \cdot xH_2O$
(Discarded)
Addition of 0.05 g Al as $AlCl_3$, NH_4Cl, and NH_4OH until alkaline, filtration, and washing
Treatment with HF, H_2SO_4, evaporation, ignition, and weighing
Precipitate
Filtrate
Compounds containing Al (Si, F, B)
(Discarded)
weight B = impurities
Solution in dilute H_2SO_4, addition of H_3BO_3, evaporation to fumes, dilution, filtration, and washing
A − B = weight of SiO_2
Filtrate
Residue (4)
(Discarded)
Compounds of (Si, B)

B. Determination of B_2O_3

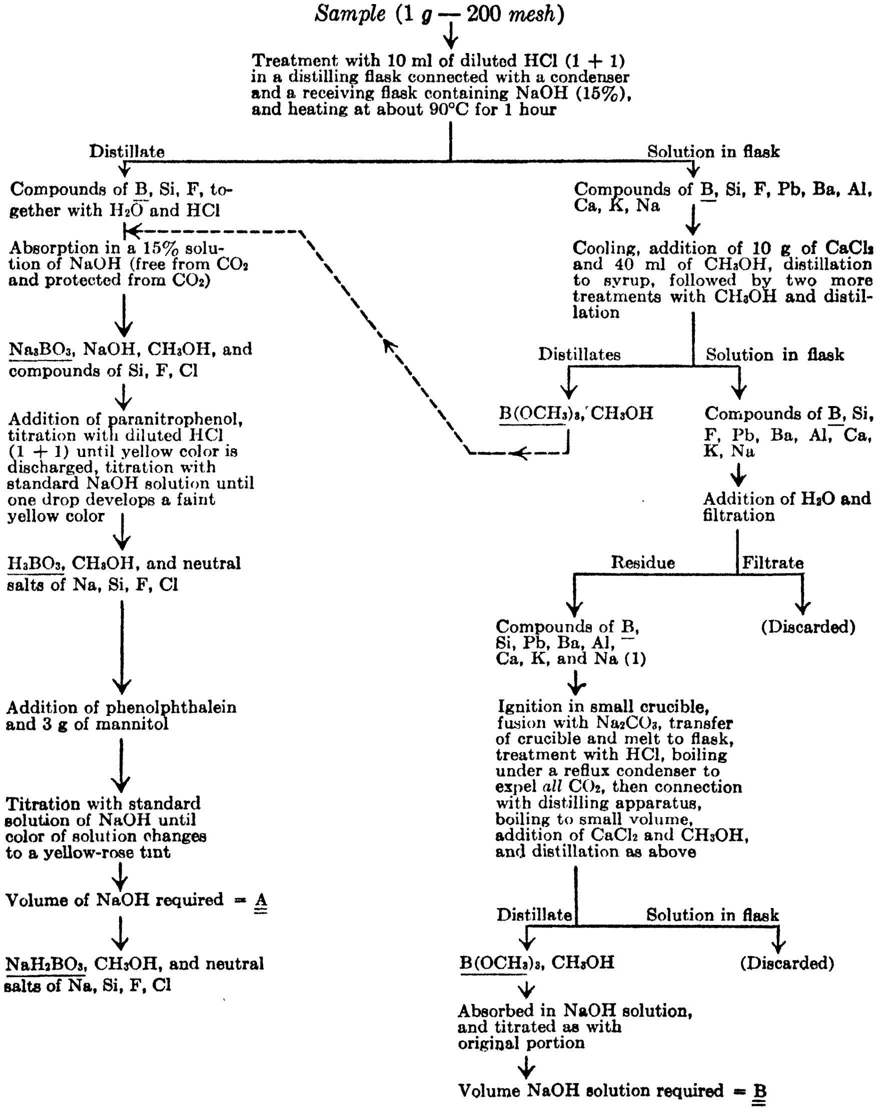
In this determination, the B_2O_3 is obtained as the very weak acid, H_3BO_3, in a solution containing no other acid, including carbonic acid. The boric acid is next converted to a stronger complex acid by adding the hexahydric alcohol, mannitol, and this is titrated with a standard alkaline solution. The determination is complicated by the presence of fluorine which necessitates special precautions to prevent loss of boron as the volatile trifluoride, BF_3, during the preliminary treatments. These are indicated in Table 96.

TABLE 96

Analysis of a Wet-process Enamel for Cast Iron (*continued*)

(SiO_2, B_2O_3, F, PbO, BaO, Al_2O_3, CaO, K_2O, Na_2O)

B. Determination of B_2O_3



Sample (1 *g* — 200 *mesh*)

Treatment with 10 ml of diluted HCl (1 + 1) in a distilling flask connected with a condenser and a receiving flask containing NaOH (15%), and heating at about 90°C for 1 hour

Distillate

Compounds of B, Si, F, together with H_2O and HCl

Absorption in a 15% solution of NaOH (free from CO_2 and protected from CO_2)

Na_3BO_3, NaOH, CH_3OH, and compounds of Si, F, Cl

Addition of paranitrophenol, titration with diluted HCl (1 + 1) until yellow color is discharged, titration with standard NaOH solution until one drop develops a faint yellow color

H_3BO_3, CH_3OH, and neutral salts of Na, Si, F, Cl

Addition of phenolphthalein and 3 g of mannitol

Titration with standard solution of NaOH until color of solution changes to a yellow-rose tint

Volume of NaOH required = A

NaH_2BO_3, CH_3OH, and neutral salts of Na, Si, F, Cl

Solution in flask

Compounds of B, Si, F, Pb, Ba, Al, Ca, K, Na

Cooling, addition of 10 g of $CaCl_2$ and 40 ml of CH_3OH, distillation to syrup, followed by two more treatments with CH_3OH and distillation

Distillates

$B(OCH_3)_3$, CH_3OH

Solution in flask

Compounds of B, Si, F, Pb, Ba, Al, Ca, K, Na

Addition of H_2O and filtration

Residue

Compounds of B, Si, Pb, Ba, Al, Ca, K, and Na [1]

Ignition in small crucible, fusion with Na_2CO_3, transfer of crucible and melt to flask, treatment with HCl, boiling under a reflux condenser to expel *all* CO_2, then connection with distilling apparatus, boiling to small volume, addition of $CaCl_2$ and CH_3OH, and distillation as above

Distillate

$B(OCH_3)_3$, CH_3OH

Absorbed in NaOH solution, and titrated as with original portion

Volume NaOH solution required = B

Solution in flask

(Discarded)

Filtrate

(Discarded)

[A + B] − volume of NaOH required in a blank run = volume of standard NaOH solution required to convert H_3BO_3 to NaH_2BO_3. B_2O_3 titer of the NaOH solution is obtained by treating weighed portions of B_2O_3 as in method.

---

[1] As a rule, this residue contains no fluorine.

C. Determination of F

Fluorine, like boron, does not enter into reactions that are selective enough to permit its direct determination in the presence of elements with which it is commonly associated. Determinations must therefore usually be preceded by more or less complicated treatments. In Table 97, the determination is made by precipitating the fluorine as lead chlorofluoride in a solution buffered at about *p*H 5 by means of sodium acetate and acetic acid

$$NaF + HCl + Pb(NO_3)_2 + NaC_2H_3O_2 = PbClF + 2\ NaNO_3 + HC_2H_3O_2$$

filtering, and dissolving the precipitate in dilute nitric acid

$$PbClF + 2\ HNO_3 = Pb(NO_3)_2 + HF + HCl$$

adding a standard solution of silver nitrate in excess

$$HCl + AgNO_3 \text{ in excess} = AgCl + HNO_3 + \text{excess of } AgNO_3$$

again filtering, and titrating the excess as in Volhard's method

$$AgNO_3 + NH_4CNS = AgCNS + NH_4NO_3$$
$$6\ NH_4CNS + Fe_2(SO_4)_3 = 2\ Fe(CNS)_3 + 3\ (NH_4)_2SO_4.$$

The different steps of the process are shown in Table 97.

NOTES

[1] Enamels containing antimony yield high results for fluorine if treated in this fashion. In such case the solution is treated with 5 g of $(NH_4)_2CO_3$ instead of a solution of zinc oxide in nitric acid, digested on a steambath for 2 hours, and filtered, and the residue is washed with a dilute solution of ammonium carbonate. The filtrate and washings are then boiled to expel ammonia, neutralized, heated with an ammoniacal solution of zinc oxide as outlined in the method for silica, filtered, and the filtrate treated with bromphenol blue, sodium chloride, and lead nitrate as usual.

[2] If desired, the filtrate obtained after the treatment with an ammoniacal solution of zinc oxide in the determination of SiO_2 (page 189) can be substituted at this point.

[3] Compounds of aluminum, boron, or large amounts of alkali salts tend to retard or prevent complete precipitation of lead chlorofluoride. The error caused by boron is negligible if the enamel contains no more than 10 per cent each of boron and fluorine.

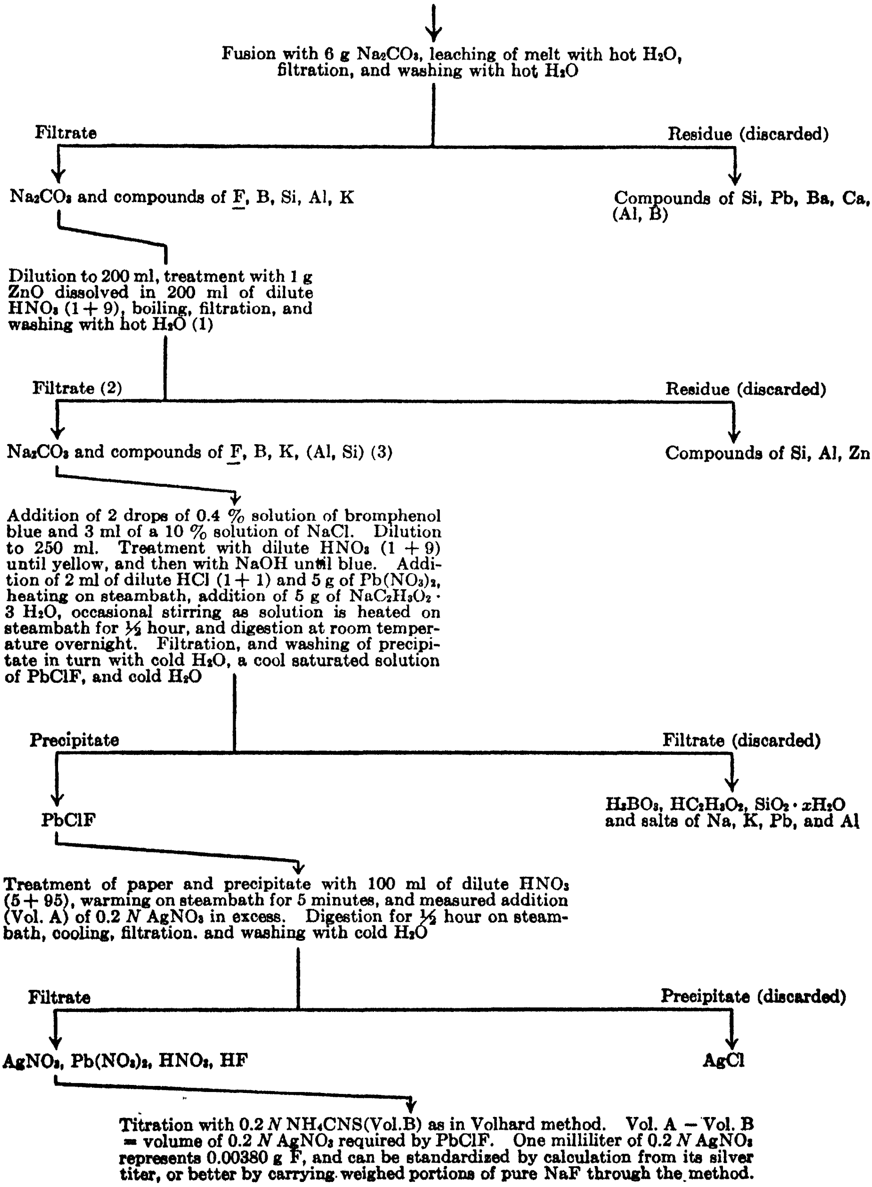
TABLE 97

Analysis of a Wet-process Enamel for Cast Iron (*continued*)

(SiO_2, B_2O_3, F, PbO, BaO, Al_2O_3, CaO, K_2O, Na_2O)

C. Determination of Fluorine

Sample (0.5 *g* — 200 *mesh*)



Fusion with 6 g Na_2CO_3, leaching of melt with hot H_2O, filtration, and washing with hot H_2O

Filtrate

Na_2CO_3 and compounds of F, B, Si, Al, K

Residue (discarded)

Compounds of Si, Pb, Ba, Ca, (Al, B)

Dilution to 200 ml, treatment with 1 g ZnO dissolved in 200 ml of dilute HNO_3 (1 + 9), boiling, filtration, and washing with hot H_2O (1)

Filtrate (2)

Na_2CO_3 and compounds of F, B, K, (Al, Si) (3)

Residue (discarded)

Compounds of Si, Al, Zn

Addition of 2 drops of 0.4 % solution of bromphenol blue and 3 ml of a 10 % solution of NaCl. Dilution to 250 ml. Treatment with dilute HNO_3 (1 + 9) until yellow, and then with NaOH until blue. Addition of 2 ml of dilute HCl (1 + 1) and 5 g of $Pb(NO_3)_2$, heating on steambath, addition of 5 g of $NaC_2H_3O_2 \cdot 3\,H_2O$, occasional stirring as solution is heated on steambath for ½ hour, and digestion at room temperature overnight. Filtration, and washing of precipitate in turn with cold H_2O, a cool saturated solution of PbClF, and cold H_2O

Precipitate

PbClF

Filtrate (discarded)

H_3BO_3, $HC_2H_3O_2$, $SiO_2 \cdot xH_2O$ and salts of Na, K, Pb, and Al

Treatment of paper and precipitate with 100 ml of dilute HNO_3 (5 + 95), warming on steambath for 5 minutes, and measured addition (Vol. A) of 0.2 *N* $AgNO_3$ in excess. Digestion for ½ hour on steambath, cooling, filtration, and washing with cold H_2O

Filtrate

$AgNO_3$, $Pb(NO_3)_2$, HNO_3, HF

Precipitate (discarded)

AgCl

Titration with 0.2 *N* NH_4CNS(Vol.B) as in Volhard method. Vol. A − Vol. B = volume of 0.2 *N* $AgNO_3$ required by PbClF. One milliliter of 0.2 *N* $AgNO_3$ represents 0.00380 g F, and can be standardized by calculation from its silver titer, or better by carrying weighed portions of pure NaF through the method.

D. Determinations of PbO, BaO, Al_2O_3, and CaO

The foregoing determinations do not leave residues or solutions that can be conveniently used in determinations of the remaining constituents. A new sample is accordingly taken and treated so as to leave a solution containing little, if any, silicon, fluorine, or boron. Still further treatments are required to remove lead and barium before the General Procedure can be applied. These are shown in Table 98.

NOTES

[1] More or less fluorine (in combination with Ba, Al, and Si) may still be left in spite of the preliminary treatment.

[2] Enamels of this type contain too much lead to permit drying and weighing of the deposit. If desired, the cold electrolyte can be treated with hydrogen sulphide to make sure that recovery of the lead is complete.

[3] If operations have been carefully performed, the barium sulphate should contain no lead sulphate. The practice of extracting lead sulphate from a mixture of lead and barium sulphates by treating with a solution containing ammonium acetate and acetic acid is not satisfactory, for some lead remains in the residue and some barium passes into solution.

[4] If the enamel contains constituents such as iron, titanium, or zirconium these will be found (as oxides) with the Al_2O_3.

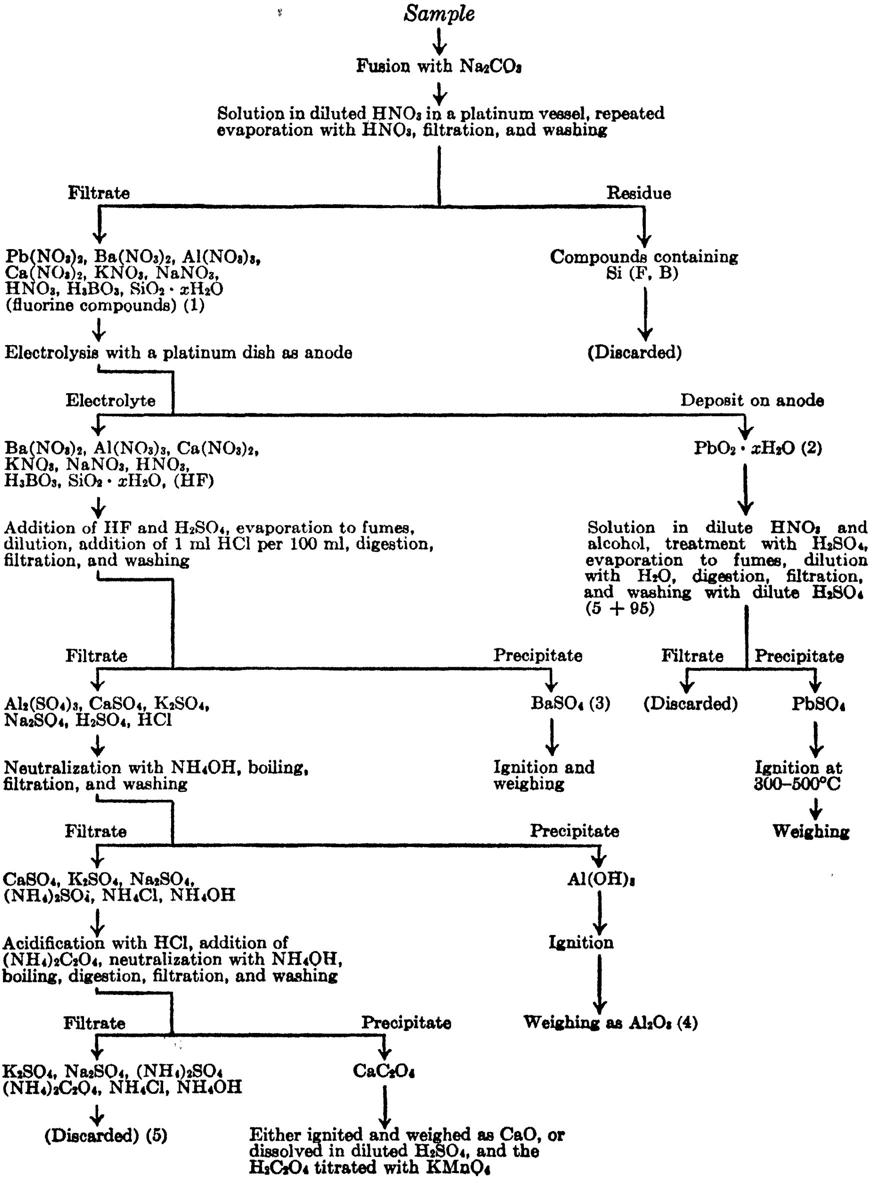
[5] Magnesium, if present in the enamel, can be determined in this filtrate. The alkalies are determined in a separate sample by the J. Lawrence Smith method, modified as directed on page 75.

TABLE 98

Analysis of a Wet-process Enamel (*continued*)

(SiO_2, B_2O_3, F, PbO, BaO, Al_2O_3, CaO, K_2O, Na_2O)

D. Determination of PbO, BaO, Al_2O_3, and CaO


Sample
Fusion with Na_2CO_3
Solution in diluted HNO_3 in a platinum vessel, repeated evaporation with HNO_3, filtration, and washing
Filtrate
Residue
$Pb(NO_3)_2$, $Ba(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, KNO_3, $NaNO_3$, HNO_3, H_3BO_3, $SiO_2 \cdot xH_2O$ (fluorine compounds) (1)
Compounds containing Si (F, B)
Electrolysis with a platinum dish as anode
(Discarded)
Electrolyte
Deposit on anode
$Ba(NO_3)_2$, $Al(NO_3)_3$, $Ca(NO_3)_2$, KNO_3, $NaNO_3$, HNO_3, H_3BO_3, $SiO_2 \cdot xH_2O$, (HF)
$PbO_2 \cdot xH_2O$ (2)
Addition of HF and H_2SO_4, evaporation to fumes, dilution, addition of 1 ml HCl per 100 ml, digestion, filtration, and washing
Solution in dilute HNO_3 and alcohol, treatment with H_2SO_4, evaporation to fumes, dilution with H_2O, digestion, filtration, and washing with dilute H_2SO_4 (5 + 95)
Filtrate
Precipitate
Filtrate
Precipitate
$Al_2(SO_4)_3$, $CaSO_4$, K_2SO_4, Na_2SO_4, H_2SO_4, HCl
$BaSO_4$ (3)
(Discarded)
$PbSO_4$
Neutralization with NH_4OH, boiling, filtration, and washing
Ignition and weighing
Ignition at 300–500°C
Weighing
Filtrate
Precipitate
$CaSO_4$, K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, NH_4Cl, NH_4OH
$Al(OH)_3$
Acidification with HCl, addition of $(NH_4)_2C_2O_4$, neutralization with NH_4OH, boiling, digestion, filtration, and washing
Ignition
Filtrate
Precipitate
Weighing as Al_2O_3 (4)
K_2SO_4, Na_2SO_4, $(NH_4)_2SO_4$, $(NH_4)_2C_2O_4$, NH_4Cl, NH_4OH
CaC_2O_4
(Discarded) (5)
Either ignited and weighed as CaO, or dissolved in diluted H_2SO_4, and the $H_2C_2O_4$ titrated with $KMnO_4$

CHAPTER XLVII

ANALYSIS OF STEEL

A. Determination of Carbon in Plain Carbon Steel

In this determination, the steel is burned in an atmosphere of oxygen, the volatile products of combustion are passed through reagents which condense or absorb everything but oxygen and carbon dioxide, and the carbon dioxide is then absorbed in a vessel which is weighed before and after the absorption takes place. The steps of the process are illustrated in Table 99.

NOTES

[1] The sample of steel must be composed of clean particles of a size that will burn readily. These are placed on a refractory bedding in a suitable boat, which is then inserted in a heated combustion tube. This is connected at one end with suitable arrangements for introducing pure oxygen, and at the other end with suitable tubes and reagents for purifying and catching the carbon dioxide formed.

[2] The required temperature ranges from 1000° to 1300°C, depending on the type of steel.

[3] The oxygen must be free from carbon dioxide and organic compounds. For this reason it is always purified by passing it through a carbon dioxide absorbent such as soda-asbestos, after it has been preheated in a tube containing copper oxide if organic matter is present.

[4] If proper conditions have been established, the residue contains so little unburned carbon that it is reburned only in the most accurate determinations.

[5] Besides carbon dioxide, the burning of the steel always gives rise to sulphur dioxide and sulphur trioxide. If the steel contains appreciable amounts of elements, such as arsenic or selenium, that form volatile oxides, these can also be expected. Finally, the gas stream will contain small amounts of water derived from the oxygen, or from the sample, the bedding, or the boat. The removal of the oxides of arsenic and selenium presents no difficulties, for their vapors condense and deposit soon after they leave the hot zone. The vapor of sulphur trioxide is not condensed as easily, and will not be removed completely unless the gas stream is subjected to an efficient scrubbing action, such as passage through columns of closely packed reagent. Sulphur dioxide, which is difficult to separate from carbon dioxide if left in the gaseous state, is removed by oxidizing it to sulphur trioxide, which can be condensed.

[6] High-sulphur steels require oxidants such as a strong solution of potassium dichromate or permanganate, or a suitably heated catalyst such as platinized silica gel. For low-sulphur steels a saturated solution of chromic acid in sulphuric acid can be used.

[7] It is of the greatest importance that the moisture content of the gases that enter the weighed vessel be the same as that of the gas that leaves it. Consequently the preliminary drying is done by a desiccant of the same power as is used in the weighed vessel.

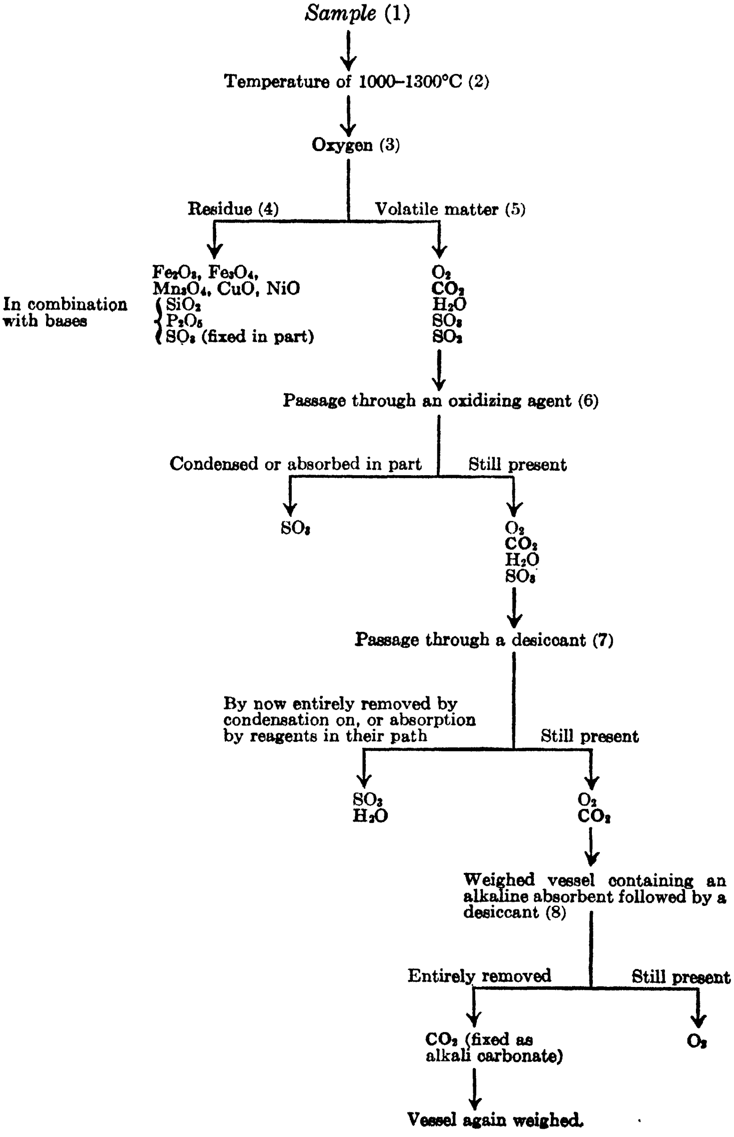
[8] The weighed absorbing vessel must contain a reagent that will absorb carbon dioxide rapidly and quantitatively, together with a desiccant that will absorb the water liberated in the reaction, and leave the escaping oxygen as dry as it was when it entered the vessel.

In addition to the elements listed, steels may contain others, such as chromium, vanadium, molybdenum, tungsten, cobalt, selenium, tin, antimony, or arsenic which have been intentionally added for alloying purposes, or accidentally introduced through ores or scrap. Some of these necessitate special treatments if they are present in appreciable amount.

TABLE 99

Determination of Carbon in Steel

(*Fe, C, Mn, P, S, Si, Cu, Ni*)


Sample (1)
Temperature of 1000–1300°C (2)
Oxygen (3)
Residue (4)
Volatile matter (5)
Fe_2O_3, Fe_3O_4,
Mn_3O_4, CuO, NiO
In combination with bases
SiO_2
P_2O_5
SO_3 (fixed in part)
O_2
CO_2
H_2O
SO_3
SO_2
Passage through an oxidizing agent (6)
Condensed or absorbed in part
Still present
SO_3
O_2
CO_2
H_2O
SO_3
Passage through a desiccant (7)
By now entirely removed by condensation on, or absorption by reagents in their path
Still present
SO_3
H_2O
O_2
CO_2
Weighed vessel containing an alkaline absorbent followed by a desiccant (8)
Entirely removed
Still present
CO_2 (fixed as alkali carbonate)
O_2
Vessel again weighed.

B. Determination of Manganese in Plain Carbon Steel

In the following method for the determination of manganese in plain carbon steels, the essential points are:

(1) The oxidation of the manganous nitrate to permanganic acid by the action of sodium bismuthate in dilute nitric acid solution

$$2\,Mn(NO_3)_2 + 5\,NaBiO_3 + 16\,HNO_3 = 2\,HMnO_4 + 5\,NaNO_3 + 5\,Bi(NO_3)_3 + 7\,H_2O.$$

(2) The reduction of the permanganic acid by the use of a standard solution of ferrous sulphate, added in excess

$$2\,HMnO_4 + 10\,FeSO_4 + 16\,HNO_3 = 2\,Mn(NO_3)_2 + 3\,Fe_2(SO_4)_3 + H_2SO_4 + 4\,Fe(NO_3)_3 + 8\,H_2O.$$

(3) The oxidation of the excess of ferrous sulphate by means of a standard solution of potassium permanganate

$$2\,KMnO_4 + 10\,FeSO_4 + 16\,HNO_3 = 2\,Mn(NO_3)_2 + K_2SO_4 + 3\,Fe_2(SO_4)_3 + 4\,Fe(NO_3)_3 + 8\,H_2O.$$

If the standard solutions of ferrous sulphate and of potassium permanganate are exactly equivalent, the difference between the volumes of each that are used represents the volume of standard permanganate that contains the same amount of manganese as the sample of steel.

The different steps of the process are shown in Table 100.

NOTES

[1] Alloy steels may require a different solvent and a different preliminary treatment.

[2] This vigorous oxidizing treatment is needed to make sure that all residual organic matter is destroyed. Ammonium persulphate is sometimes substituted for sodium bismuthate.

[3] This reducing treatment is necessary for the reduction of chromic acid, and to dissolve any oxidized manganese compounds that may have separated from solution through decomposition of permanganic acid during the vigorous boiling. Chromic acid is always present at this stage, for chromium, which is present in all steels, is oxidized to the sexivalent state when treated with bismuthate or permanganic acid in *boiling* dilute nitric acid solution.

[4] More or less of the chromium will be present as chromic acid at this stage and will oxidize ferrous sulphate in the next step, thus causing high results for manganese. The oxidation of chromium by bismuthate or permanganic acid proceeds so slowly in *cold* solution that moderate amounts of it (0.25 per cent or less) cause insignificant errors. With higher percentages another method must be used, or else the manganese must be separated from the chromium before treating with bismuthate.

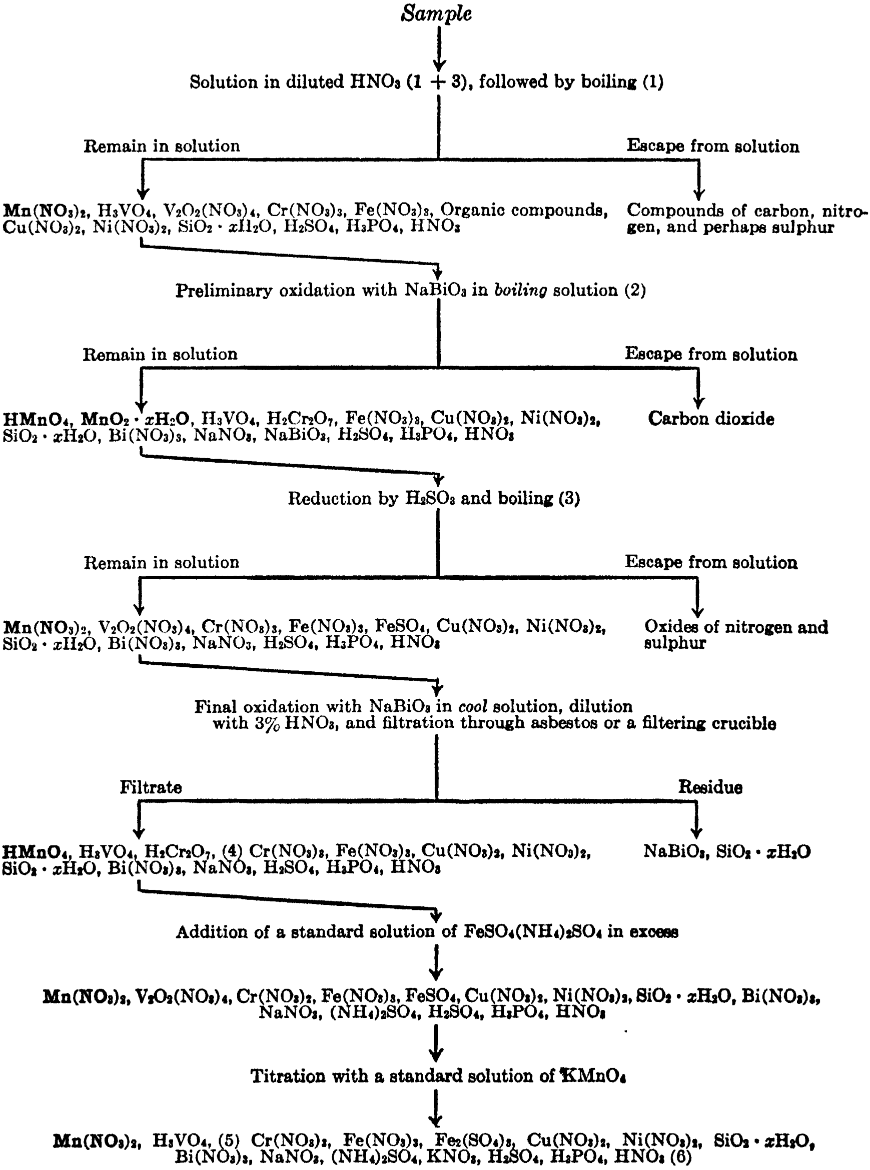
[5] Any vanadium present in the steel is oxidized to the quinquevalent state by bismuthate, reduced to the quadrivalent state by ferrous sulphate, and then reoxidized so slowly by the permanganate that it causes a "fading" end point. The addition of permanganate must then be continued until the pink color persists after stirring for about 30 seconds.

[6] It is interesting to note the rather large number of compounds that have accumulated in solution in the course of this comparatively simple determination.

TABLE 100

Determination of Manganese in Plain Carbon Steel

(Fe, C, Mn, P, S, Si, Cu, Ni, Cr, V)



Sample

Solution in diluted HNO_3 (1 + 3), followed by boiling (1)

Remain in solution

$Mn(NO_3)_2$, H_3VO_4, $V_2O_2(NO_3)_4$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, Organic compounds, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, H_2SO_4, H_3PO_4, HNO_3

Escape from solution

Compounds of carbon, nitrogen, and perhaps sulphur

Preliminary oxidation with $NaBiO_3$ in *boiling* solution (2)

Remain in solution

$HMnO_4$, $MnO_2 \cdot xH_2O$, H_3VO_4, $H_2Cr_2O_7$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, $Bi(NO_3)_3$, $NaNO_3$, $NaBiO_3$, H_2SO_4, H_3PO_4, HNO_3

Escape from solution

Carbon dioxide

Reduction by H_2SO_3 and boiling (3)

Remain in solution

$Mn(NO_3)_2$, $V_2O_2(NO_3)_4$, $Cr(NO_3)_3$, $Fe(NO_3)_3$, $FeSO_4$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, $Bi(NO_3)_3$, $NaNO_3$, H_2SO_4, H_3PO_4, HNO_3

Escape from solution

Oxides of nitrogen and sulphur

Final oxidation with $NaBiO_3$ in *cool* solution, dilution with 3% HNO_3, and filtration through asbestos or a filtering crucible

Filtrate

$HMnO_4$, H_3VO_4, $H_2Cr_2O_7$, (4) $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, $Bi(NO_3)_3$, $NaNO_3$, H_2SO_4, H_3PO_4, HNO_3

Residue

$NaBiO_3$, $SiO_2 \cdot xH_2O$

Addition of a standard solution of $FeSO_4(NH_4)_2SO_4$ in excess

$Mn(NO_3)_2$, $V_2O_2(NO_3)_4$, $Cr(NO_3)_2$, $Fe(NO_3)_3$, $FeSO_4$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, $Bi(NO_3)_3$, $NaNO_3$, $(NH_4)_2SO_4$, H_2SO_4, H_3PO_4, HNO_3

Titration with a standard solution of $KMnO_4$

$Mn(NO_3)_2$, H_3VO_4, (5) $Cr(NO_3)_3$, $Fe(NO_3)_3$, $Fe_2(SO_4)_3$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, $SiO_2 \cdot xH_2O$, $Bi(NO_3)_3$, $NaNO_3$, $(NH_4)_2SO_4$, KNO_3, H_2SO_4, H_3PO_4, HNO_3 (6)

C. Determination of Phosphorus in Plain Carbon Steel

Practically all the phosphorus in plain carbon steels occurs in combination with iron as phosphide. These are converted to ferric nitrate and orthophosphoric acid by dissolving the steel in diluted nitric acid, after which the phosphorus is precipitated as ammonium phosphomolybdate. In analyses of the highest accuracy, the precipitate is dissolved in ammonium hydroxide and the phosphorus precipitated twice as magnesium ammonium phosphate, which is converted to magnesium pyrophosphate and weighed. In ordinary analyses, the ammonium phosphomolybdate precipitate is dissolved in an excess of a standard solution of sodium hydroxide, the solution titrated with a standard solution of nitric acid, and the phosphorus content calculated from the volume of alkaline solution that was required to react with the ammonium phosphomolybdate. These procedures are illustrated in Table 101.

NOTES

[1] Some alloy steels require special solvents. These must always be oxidizing, for otherwise much if not all of the phosphorus will be volatilized and lost as volatile hydrides of phosphorus. The action of nitric acid can be illustrated by the following equation:

$$3\ Fe_3P + 41\ HNO_3 = 9\ Fe(NO_3)_3 + 3\ H_3PO_4 + 14\ NO + 16\ H_2O.$$

If the attack leaves a residue, as with high-silicon, tungsten, titanium, or zirconium steels, this must be examined for a possible phosphorus content.

[2] If the steel contains arsenic or vanadium, these are present as arsenic and vanadic acids at this stage. The former does not retard precipitation, and little if any of it is precipitated as ammonium arsenomolybdate if the temperature does not exceed 40°C. Vanadic acid, on the other hand, both retards precipitation and contaminates the precipitate. If present in appreciable amounts, as in vanadium steels, it must be reduced to the quadrivalent stage, and the precipitation must be made at 15–20°C. The precipitation of ammonium phosphomolybdate can be illustrated as follows:

$$H_3PO_4 + 12\ H_2MoO_4 + 3\ NH_4NO_3 = (NH_4)_3PO_4 \cdot 12\ MoO_3 + 3\ HNO_3 + 12\ H_2O.$$

Silicic acid is objectionable; large amounts are removed by filtration, small amounts by adding a few drops of hydrofluoric acid and boiling.

[3] This method is widely used in routine determinations of phosphorus. The reactions upon which it is based are illustrated by the following equations:

$$(NH_4)_3PO_4 \cdot 12\ MoO_3 + 27\ NaOH = Na_3PO_4 + 12\ Na_2MoO_4 + 3\ NH_4OH + 12\ H_2O$$

$$Na_3PO_4 + 12\ Na_2MoO_4 + 3\ NH_4OH + 4\ HNO_3 =$$
$$Na_2HPO_4 + NH_4NaMoO_4 + (NH_4)_2MoO_4 + 10\ Na_2MoO_4 + 4\ NaNO_3 + 3\ H_2O$$

$$NaOH(excess) + HNO_3 = NaNO_3 + H_2O.$$

In another volumetric method, that was widely used some years ago, the molybdenum in the precipitate is reduced to the trivalent state in a Jones reductor (page 149), and the percentage of phosphorus is calculated from the volume of permanganate required to reoxidize it to the sexivalent condition.

[4] The " phosphorus titer " of the NaOH solution can be determined by carrying a steel of known phosphorus content through all steps of the process. If proper conditions are established, it can be calculated from the " sodium hydroxide " titer of the solution by assuming that 1 molecule of $(NH_4)_3PO_4 \cdot 12\ MoO_3$ requires 23 molecules of NaOH, or $1\ P = 23\ NaOH$.

[5] This method is based on the following reactions:

$$(NH_4)_3PO_4 \cdot 12\,MoO_3 + 24\,NH_4OH = (NH_4)_3PO_4 + 12\,(NH_4)_2MoO_4 + 12\,H_2O$$
$$(NH_4)_3PO_4 + MgCl_2 + 6\,H_2O = MgNH_4PO_4 \cdot 6\,H_2O + 2\,NH_4Cl$$
$$2\,MgNH_4PO_4 \cdot 6\,H_2O + \text{heat} = Mg_2P_2O_7 + 2\,NH_3 + 7\,H_2O.$$

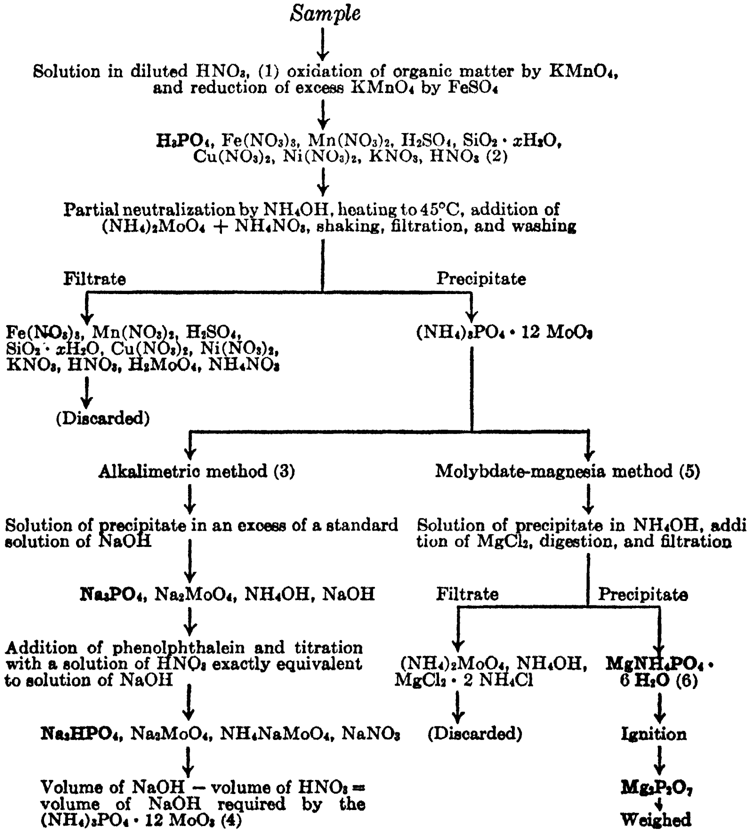
In another method, which is not quite so accurate, the molybdenum in the ammonium phosphomolybdate is precipitated and weighed as lead molybdate, $PbMoO_4$, and the amount of phosphorus is then calculated from the ratio 1 P : 12 $PbMoO_4$. In other methods, which are also less accurate than the molybdate-magnesia method, the phosphomolybdate precipitate is dried and weighed as such, or ignited at about 450°C and weighed as $P_2O_5 \cdot 24\,MoO_3$.

[6] In determinations of the highest accuracy, the precipitate is dissolved in a little dilute hydrochloric acid, and the phosphorus again precipitated by adding a very little $MgCl_2$ and then ammonium hydroxide in excess. Two precipitations of the magnesium ammonium phosphate are needed to make sure that all the molybdenum has been removed and that the precipitate is of proper composition.

TABLE 101

Determination of Phosphorus in Plain Carbon Steel

(*Fe, C, Mn, P, S, Si, Cu, Ni*)



Sample

Solution in diluted HNO_3, (1) oxidation of organic matter by $KMnO_4$, and reduction of excess $KMnO_4$ by $FeSO_4$

H_3PO_4, $Fe(NO_3)_3$, $Mn(NO_3)_2$, H_2SO_4, $SiO_2 \cdot xH_2O$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, KNO_3, HNO_3 (2)

Partial neutralization by NH_4OH, heating to 45°C, addition of $(NH_4)_2MoO_4 + NH_4NO_3$, shaking, filtration, and washing

Filtrate

$Fe(NO_3)_3$, $Mn(NO_3)_2$, H_2SO_4, $SiO_2 \cdot xH_2O$, $Cu(NO_3)_2$, $Ni(NO_3)_2$, KNO_3, HNO_3, H_2MoO_4, NH_4NO_3

(Discarded)

Precipitate

$(NH_4)_3PO_4 \cdot 12\,MoO_3$

Alkalimetric method (3)

Solution of precipitate in an excess of a standard solution of NaOH

Na_3PO_4, Na_2MoO_4, NH_4OH, NaOH

Addition of phenolphthalein and titration with a solution of HNO_3 exactly equivalent to solution of NaOH

Na_2HPO_4, Na_2MoO_4, NH_4NaMoO_4, $NaNO_3$

Volume of NaOH − volume of HNO_3 = volume of NaOH required by the $(NH_4)_3PO_4 \cdot 12\,MoO_3$ (4)

Molybdate-magnesia method (5)

Solution of precipitate in NH_4OH, addition of $MgCl_2$, digestion, and filtration

Filtrate

$(NH_4)_2MoO_4$, NH_4OH, $MgCl_2 \cdot 2\,NH_4Cl$

(Discarded)

Precipitate

$MgNH_4PO_4 \cdot 6\,H_2O$ (6)

Ignition

$Mg_2P_2O_7$

Weighed

D. Determination of Chromium in Chromium-Vanadium Steel

In this determination, which illustrates the rapid volumetric methods often used in analyses of metallurgical materials, the sample of steel is dissolved in a mixture of diluted sulphuric and phosphoric acids, and the solution is then treated in succession with (1) nitric acid, (2) silver nitrate and ammonium persulphate, (3) diluted hydrochloric acid, (4) a standard solution of ferrous sulphate, and (5) a standard solution of potassium permanganate. The steps of the process are illustrated in Table 102.

NOTES

[1] A mixture of diluted sulphuric and phosphoric acids is the solvent instead of the commonly used diluted nitric acid because it dissolves all types of chromium steels, and the phosphoric acid decolorizes the iron salts that are formed.

[2] Evaporation with nitric acid is necessary to break up the black insoluble carbides of chromium and vanadium left after the non-oxidizing attack with the mixed acids. Steels containing considerable silicon may leave a residue of white silicic acid; steels containing tungsten may leave a residue of yellow tungstic acid. Small amounts of chromium and vanadium are retained by the latter, and must be recovered in analyses of high accuracy.

[3] The treatment with persulphate and silver nitrate serves to oxidize chromium to the sexivalent state

$$Cr_2(SO_4)_3 + 3\,(NH_4)_2S_2O_8 + 8\,H_2O = 2\,H_2CrO_4 + 3\,(NH_4)_2SO_4 + 6\,H_2SO_4$$

and unoxidized vanadium to the quinquevalent state

$$V_2O_2(SO_4)_2 + (NH_4)_2S_2O_8 + 6\,H_2O = 2\,H_3VO_4 + (NH_4)_2SO_4 + 3\,H_2SO_4.$$

Manganese is oxidized as well, first to permanganic acid

$$2\,MnSO_4 + 5\,(NH_4)_2S_2O_8 + 8\,H_2O = 2\,HMnO_4 + 5\,(NH_4)_2SO_4 + 7\,H_2SO_4.$$

[4] Vigorous boiling is necessary to destroy completely the persulphate still left in solution

$$2\,(NH_4)_2S_2O_8 + 2\,H_2O + \text{heat} = 2\,(NH_4)_2SO_4 + 2\,H_2SO_4 + O_2$$

which would otherwise cause reduction of chromic acid later. The boiling usually causes partial reduction of the permanganic acid

$$4\,HMnO_4 + (H_2O) + \text{boiling} = 4\,MnO_2 \cdot (x\,H_2O) + 3\,O_2.$$

[5] The treatment with diluted hydrochloric acid is required to destroy the oxidized manganese compounds

$$2\,HMnO_4 + 14\,HCl = 2\,MnCl_2 + 5\,Cl_2 + 8\,H_2O$$
$$MnO_2 \cdot (x\,H_2O) + 4\,HCl = MnCl_2 + Cl_2 + (x + 2\,H_2O)$$

and vigorous boiling is necessary to remove the chlorine that is formed.

[6] Ferrous sulphate is always added in excess. It reduces chromium from a valence of 6 to a valence of 3

$$2\,H_2CrO_4 + 6\,FeSO_4 + 6\,H_2SO_4 = Cr_2(SO_4)_3 + 3\,Fe_2(SO_4)_3 + 8\,H_2O$$

and vanadium from a valence of 5 to a valence of 4

$$2\,H_3VO_4 + 2\,FeSO_4 + 3\,H_2SO_4 = V_2O_2(SO_4)_2 + Fe_2(SO_4)_3 + 6\,H_2O.$$

[7] In the back titration with potassium permanganate the reduced vanadium is reoxidized

$$5\,V_2O_2(SO_4)_2 + 2\,KMnO_4 + 22\,H_2O = 10\,H_3VO_4 + K_2SO_4 + 2\,MnSO_4 + 7\,H_2SO_4$$

as is also the excess of ferrous sulphate

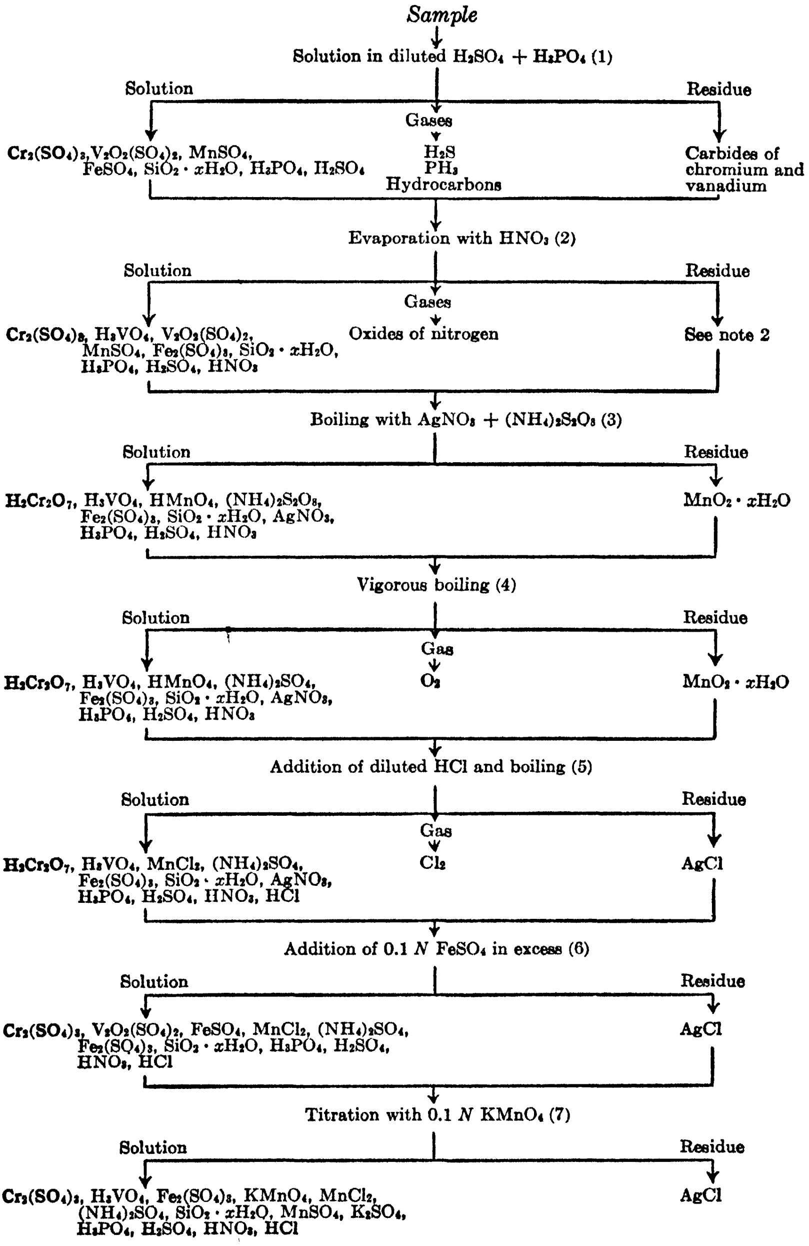
$$10\,FeSO_4 + 2\,KMnO_4 + 8\,H_2SO_4 = 5\,Fe_2(SO_4)_3 + 2\,MnSO_4 + K_2SO_4 + 8\,H_2O.$$

It is therefore apparent (1) that the sole function of the permanganate is to take care of the excess of ferrous sulphate and of the vanadium that has been reduced, and (2) that, if the solutions of ferrous sulphate and permanganate are of equal strength, the difference between the volumes used represents the volume of ferrous sulphate solution required to reduce the chromic acid formed from the chromium present in the sample of steel.

TABLE 102

Determination of Chromium in Chromium-Vanadium Steel

(Fe, C, Mn, P, S, Si, Cr, V)


Sample
Solution in diluted H_2SO_4 + H_3PO_4 (1)
Solution
Gases
Residue
$Cr_2(SO_4)_3$, $V_2O_2(SO_4)_2$, $MnSO_4$, $FeSO_4$, $SiO_2 \cdot xH_2O$, H_3PO_4, H_2SO_4
H_2S
PH_3
Hydrocarbons
Carbides of chromium and vanadium
Evaporation with HNO_3 (2)
Solution
Gases
Residue
$Cr_2(SO_4)_3$, H_3VO_4, $V_2O_2(SO_4)_2$, $MnSO_4$, $Fe_2(SO_4)_3$, $SiO_2 \cdot xH_2O$, H_3PO_4, H_2SO_4, HNO_3
Oxides of nitrogen
See note 2
Boiling with $AgNO_3$ + $(NH_4)_2S_2O_8$ (3)
Solution
Residue
$H_2Cr_2O_7$, H_3VO_4, $HMnO_4$, $(NH_4)_2S_2O_8$, $Fe_2(SO_4)_3$, $SiO_2 \cdot xH_2O$, $AgNO_3$, H_3PO_4, H_2SO_4, HNO_3
$MnO_2 \cdot xH_2O$
Vigorous boiling (4)
Solution
Gas
Residue
$H_2Cr_2O_7$, H_3VO_4, $HMnO_4$, $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $SiO_2 \cdot xH_2O$, $AgNO_3$, H_3PO_4, H_2SO_4, HNO_3
O_2
$MnO_2 \cdot xH_2O$
Addition of diluted HCl and boiling (5)
Solution
Gas
Residue
$H_2Cr_2O_7$, H_3VO_4, $MnCl_2$, $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $SiO_2 \cdot xH_2O$, $AgNO_3$, H_3PO_4, H_2SO_4, HNO_3, HCl
Cl_2
$AgCl$
Addition of 0.1 *N* $FeSO_4$ in excess (6)
Solution
Residue
$Cr_2(SO_4)_3$, $V_2O_2(SO_4)_2$, $FeSO_4$, $MnCl_2$, $(NH_4)_2SO_4$, $Fe_2(SO_4)_3$, $SiO_2 \cdot xH_2O$, H_3PO_4, H_2SO_4, HNO_3, HCl
$AgCl$
Titration with 0.1 *N* $KMnO_4$ (7)
Solution
Residue
$Cr_2(SO_4)_3$, H_3VO_4, $Fe_2(SO_4)_3$, $KMnO_4$, $MnCl_2$, $(NH_4)_2SO_4$, $SiO_2 \cdot xH_2O$, $MnSO_4$, K_2SO_4, H_3PO_4, H_2SO_4, HNO_3, HCl
$AgCl$

E. Determination of Vanadium in Chromium-Vanadium Steel

The following procedure illustrates another of the rapid volumetric methods of controlling the manufacture of metallurgical products. In this method, the steel is dissolved in a mixture of diluted sulphuric and phosphoric acids and treated as in the Determination of Chromium (page 202) until the solution has been titrated with the standard solution of potassium permanganate. After the end point has been obtained, the *cool* solution is treated with more than enough ferrous sulphate to reduce the vanadium to the quadrivalent state, and then with more than enough ammonium persulphate to oxidize the excess of ferrous sulphate. The solution is then titrated with a standard solution of potassium permanganate until the end point persists after stirring for one minute.

It should be noted that all reactions take place in a *cool* acid solution of the steel which contains *no* soluble silver salt. Under these conditions the ferrous sulphate reacts only with the vanadic acid, the persulphate reacts only with the ferrous sulphate, and the permanganate reacts only with the reduced vanadium compound. The steps of the process are illustrated in Table 103.

NOTES

[1] The addition of ferrous sulphate in excess causes reduction of the vanadium to the quadrivalent state

$$2\,H_3VO_4 + 3\,H_2SO_4 + 2\,FeSO_4 = V_2O_2(SO_4)_2 + Fe_2(SO_4)_3 + 6\,H_2O$$

and no changes occur in the valences of the other elements, except for the permanganate that was required to yield an end point in the preceding determination of chromium.

[2] In the cool solution, and in the absence of a *soluble* silver salt, ammonium persulphate does not react with the quadrivalent compound of vanadium formed in the preceding treatment, neither does it react with the trivalent chromium or divalent manganese compounds present. It does, however, quantitatively oxidize the ferrous sulphate left in solution

$$2\,FeSO_4 + (NH_4)_2S_2O_8 = Fe_2(SO_4)_3 + (NH_4)_2SO_4.$$

The net result of the two treatments therefore is the reduction of the vanadium to the quadrivalent state.

[3] No significant oxidation of chromium or decomposition of persulphate occurs in the short time allowed for the development of the end point with permanganate in the cool solution. The volume of permanganate used is therefore that required to oxidize the vanadium from the quadrivalent to the quinquevalent state

$$5\,V_2O_2(SO_4)_2 + H_2SO_4 + 2\,KMnO_4 + 22\,H_2O = 10\,H_3VO_4 + K_2SO_4 + 2\,MnSO_4 + 8\,H_2SO_4.$$

If desired, both chromium and vanadium can be determined by potentiometric methods (see page 163). In these, the end point is found by recording the changes of voltage as the titration proceeds or, in the simplest procedure, by adjusting the resistance so that the beam of a reflecting galvanometer is centered on the scale and then observing the deflection of the beam. The change in voltage is more pronounced in passing from the oxidized to the reduced form, and so the end point is found by titrating to marked change of potential, first with a standard solution of ferrous sulphate, then with a standard (preferably equivalent) solution of potassium dichromate, and finally with dropwise additions of the solution of ferrous sulphate.

TABLE 103

Determination of Vanadium in Chromium-Vanadium Steel

(In solution left after the determination of chromium, page 203)

Solution

H_3VO_4, $KMnO_4$, $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $MnCl_2$, $(NH_4)_2SO_4$,
$SiO_2 \cdot xH_2O$, $MnSO_4$, K_2SO_4, $AgCl$,
H_3PO_4, H_2SO_4, HNO_3, HCl

↓

Addition of $FeSO_4$ in moderate excess (1)

$V_2O_2(SO_4)_2$, $Cr_2(SO_4)_3$, $FeSO_4$, $Fe_2(SO_4)_3$, $MnCl_2$, $(NH_4)_2SO_4$,
$SiO_2 \cdot xH_2O$, $MnSO_4$, K_2SO_4, $AgCl$,
H_3PO_4, H_2SO_4, HNO_3, HCl

↓

Addition of $(NH_4)_2S_2O_8$ in moderate excess (2)

$V_2O_2(SO_4)_2$, $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $(NH_4)_2S_2O_8$, $MnCl_2$, $(NH_4)_2SO_4$,
$SiO_2 \cdot xH_2O$, $MnSO_4$, K_2SO_4, $AgCl$,
H_3PO_4, H_2SO_4, HNO_3, HCl

↓

Titration with a standard solution of $KMnO_4$ (3)

H_3VO_4, $KMnO_4$, $Cr_2(SO_4)_3$, $Fe_2(SO_4)_3$, $(NH_4)_2S_2O_8$, $MnCl_2$, $(NH_4)_2SO_4$,
$SiO_2 \cdot xH_2O$, $MnSO_4$, K_2SO_4, $AgCl$,
H_3PO_4, H_2SO_4, HNO_3, HCl

CHAPTER XLVIII

ANALYSIS OF BRASS

The chief components of brass are copper and zinc, in proportions which may range from *20* to *98* per cent of the former, and *2* to *80* per cent of the latter. In addition, brasses may contain other constituents, such as tin, lead, iron, and nickel (see page 18). If an alloy contains only copper and zinc, the sample is dissolved in diluted nitric acid, the solution electrolyzed (page 169), and the copper deposit weighed. After suitable treatments, the electrolyte is then treated with hydrogen sulphide to precipitate the zinc as sulphide, which is ignited to the oxide and weighed. The steps of the process are illustrated in Table 104.

NOTES

[1] The formation of a white insoluble residue at this stage would indicate the presence of tin or antimony.

[2] Pure copper has a characteristic color, which is usually changed to a marked extent if other elements have been deposited with it.

[3] The color of zinc sulphide is pure white. A dark-colored precipitate usually indicates the presence of copper which has escaped electrodeposition.

[4] The ignition of zinc sulphide to zinc oxide requires care, for it is reduced to metal if it is heated to redness while carbon is still present. Moreover, the final ignition must be done at 900°–950°C, for lower temperatures will not completely decompose the zinc sulphate formed at first, whereas higher temperatures cause volatilization of zinc oxide.

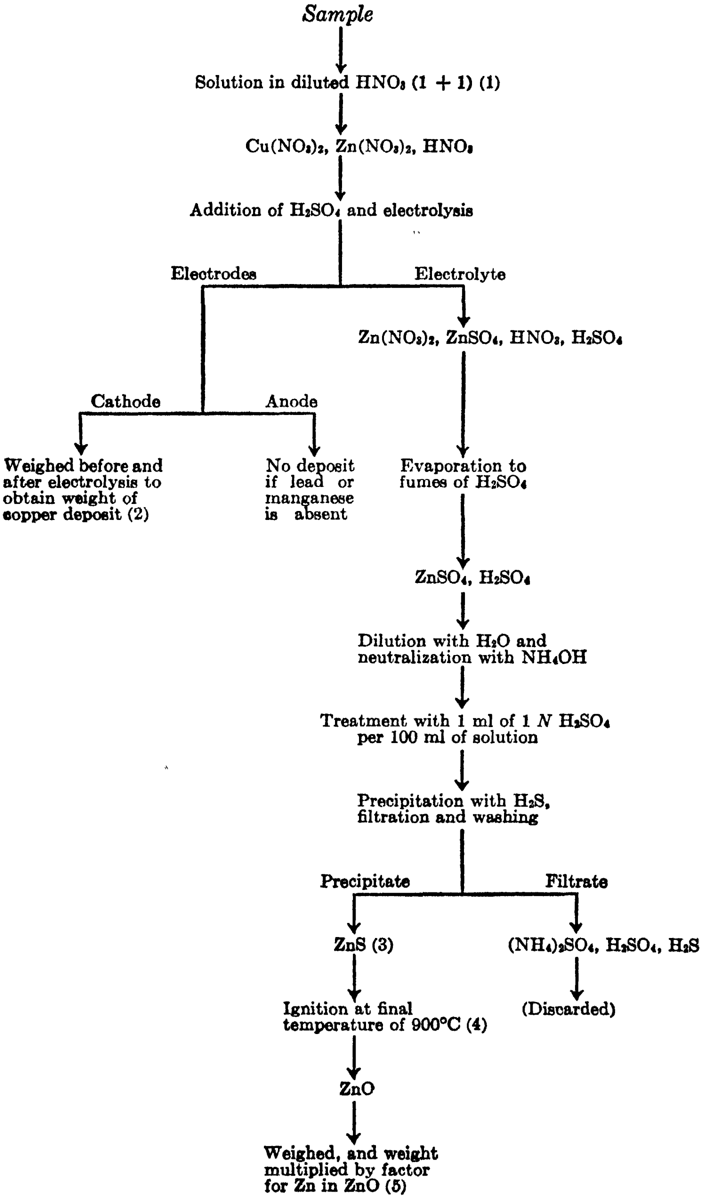
[5] In routine analyses of alloys whose components are known, the percentage of zinc is often obtained by "difference" after the percentages of the other components have been determined.

TABLE 104

Analysis of Brass

(Cu, Zn)

Determination of Copper and Zinc


Sample
Solution in diluted HNO_3 (1 + 1) (1)
$Cu(NO_3)_2$, $Zn(NO_3)_2$, HNO_3
Addition of H_2SO_4 and electrolysis
Electrodes
Electrolyte
$Zn(NO_3)_2$, $ZnSO_4$, HNO_3, H_2SO_4
Cathode
Anode
Weighed before and after electrolysis to obtain weight of copper deposit (2)
No deposit if lead or manganese is absent
Evaporation to fumes of H_2SO_4
$ZnSO_4$, H_2SO_4
Dilution with H_2O and neutralization with NH_4OH
Treatment with 1 ml of 1 *N* H_2SO_4 per 100 ml of solution
Precipitation with H_2S, filtration and washing
Precipitate
Filtrate
ZnS (3)
$(NH_4)_2SO_4$, H_2SO_4, H_2S
Ignition at final temperature of 900°C (4)
(Discarded)
ZnO
Weighed, and weight multiplied by factor for Zn in ZnO (5)

CHAPTER XLIX

ANALYSIS OF GERMAN SILVER

The chief components of German silver are copper (46 to 63 per cent), zinc (20 to 34 per cent), and nickel (6 to 25 per cent). In addition, these alloys may contain other constituents such as lead and iron.

The first part of the analysis of a German silver containing copper, nickel, zinc, lead, and iron can be made as described under brass (page 207), except that conditions are established so that lead is deposited on the anode at the same time that copper is deposited on the cathode. As in the analysis of brass, zinc is next precipitated as the sulphide after suitable treatment of the electrolyte. The filtrate left after the removal of the sulphide contains the iron (as ferrous sulphate) and the nickel. This is treated with an oxidizing agent to convert the iron to the ferric state, neutralized with ammonium hydroxide to precipitate the iron hydroxide, and filtered, and the precipitate is ignited to obtain the iron as ferric oxide. The filtrate is then made more strongly ammoniacal, and the nickel deposited by electrolysis. The steps of the process are illustrated in Table 105.

NOTES

[1] The formation of a white precipitate at this point indicates the presence of tin or antimony.

[2] No sulphuric acid is added to the electrolyte when lead is present, and a sand-blasted gauze anode is used in order to make sure that the deposit will adhere. The deposit is a hydrated dioxide which must be dried at 175°–200°C, before it is weighed.

[3] Pure copper has a characteristic color, which is usually changed to a marked extent if other elements have been deposited with it.

[4] A white residue at this point indicates that the electrodeposition of lead was incomplete and that the lead is appearing here as the sulphate.

[5] If the precipitate is dark colored instead of white, it is usually contaminated by copper or lead, as sulphides, which have crept through the preceding operations. To guard against this contingency, as well as to recover copper and lead, treatment with hydrogen sulphide can be first done in fairly strong acid (0.3 *N*) solution. If a precipitate appears, the solution is filtered, the precipitate examined for copper and lead, and the filtrate boiled to expel hydrogen sulphide before it is rendered 0.01 *N*.

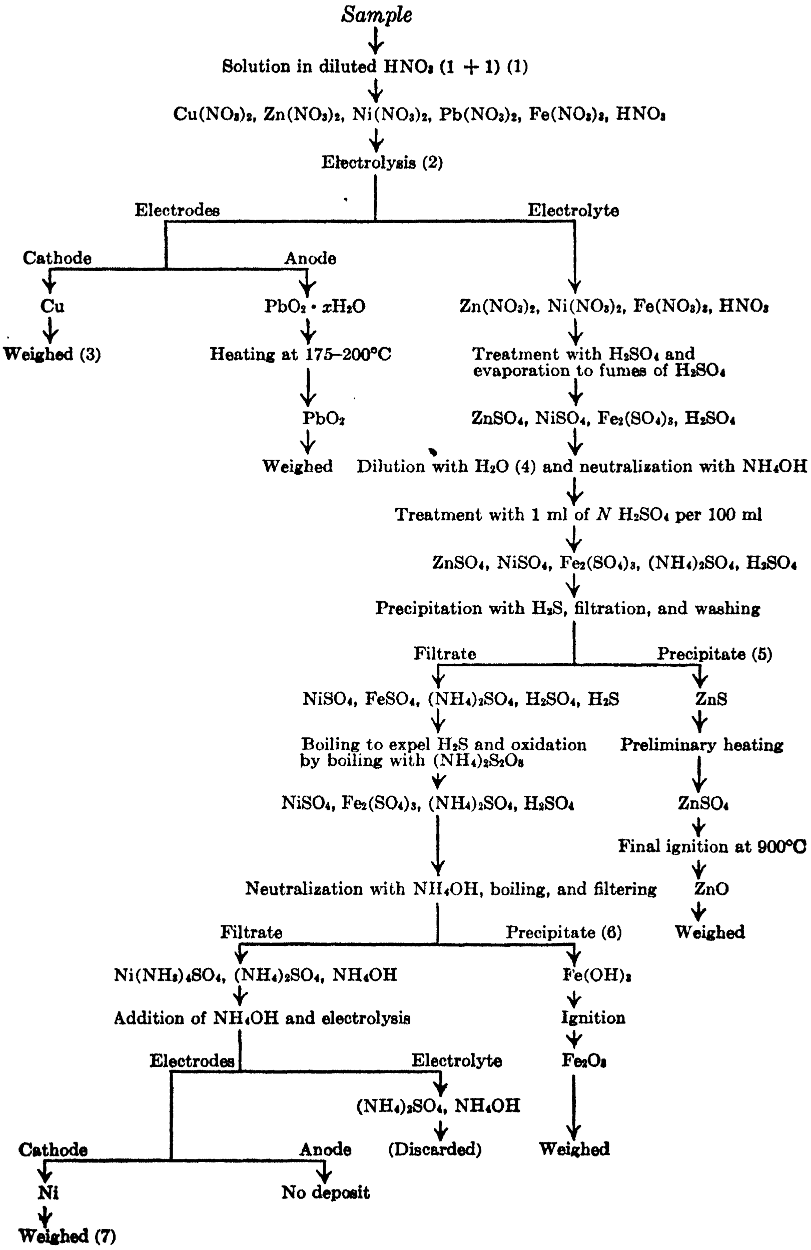
[6] In determinations of the highest accuracy, the ferric hydroxide is dissolved, reprecipitated, and filtered, and the filtrates are combined in order to recover any nickel that might have been carried down by the first precipitate.

[7] The deposit will contain any zinc that may have escaped precipitation as the sulphide, and in addition any other elements in the alloy, such as cobalt, that have survived the treatments and can be deposited under these conditions.

TABLE 105

Analysis of German Silver

(Cu, Zn, Ni, Pb, and Fe)


Sample
Solution in diluted HNO_3 (1 + 1) (1)
$Cu(NO_3)_2$, $Zn(NO_3)_2$, $Ni(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, HNO_3
Electrolysis (2)
Electrodes
Electrolyte
Cathode
Anode
Cu
Weighed (3)
$PbO_2 \cdot xH_2O$
Heating at 175–200°C
PbO_2
Weighed
$Zn(NO_3)_2$, $Ni(NO_3)_2$, $Fe(NO_3)_3$, HNO_3
Treatment with H_2SO_4 and evaporation to fumes of H_2SO_4
$ZnSO_4$, $NiSO_4$, $Fe_2(SO_4)_3$, H_2SO_4
Dilution with H_2O (4) and neutralization with NH_4OH
Treatment with 1 ml of *N* H_2SO_4 per 100 ml
$ZnSO_4$, $NiSO_4$, $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, H_2SO_4
Precipitation with H_2S, filtration, and washing
Filtrate
Precipitate (5)
$NiSO_4$, $FeSO_4$, $(NH_4)_2SO_4$, H_2SO_4, H_2S
Boiling to expel H_2S and oxidation by boiling with $(NH_4)_2S_2O_8$
$NiSO_4$, $Fe_2(SO_4)_3$, $(NH_4)_2SO_4$, H_2SO_4
ZnS
Preliminary heating
$ZnSO_4$
Final ignition at 900°C
ZnO
Weighed
Neutralization with NH_4OH, boiling, and filtering
Filtrate
Precipitate (6)
$Ni(NH_3)_4SO_4$, $(NH_4)_2SO_4$, NH_4OH
Addition of NH_4OH and electrolysis
Electrodes
Electrolyte
$(NH_4)_2SO_4$, NH_4OH
(Discarded)
Cathode
Anode
Ni
Weighed (7)
No deposit
$Fe(OH)_3$
Ignition
Fe_2O_3
Weighed

CHAPTER L

ANALYSIS OF BRONZE

The chief components of bronze are copper and tin, in proportions ranging from *50* to *97* per cent of the former, to *1* to *35* per cent of the latter. In addition, bronzes may contain other constituents, such as zinc, lead, iron, and nickel (see page 18). In most methods for the analysis of bronzes, the sample is dissolved in diluted nitric acid. This causes precipitation of the tin as metastannic acid, but unfortunately the precipitate always carries down more or less of the other elements that are present, and under some conditions precipitation of the tin is not complete.

A. Routine Analysis

In routine analyses of bronzes containing but little iron the sources of error that have been discussed are often ignored, and the metastannic acid is either ignited to the oxide and weighed, or dissolved and its tin content determined volumetrically as shown in Table 106.

NOTES

[1] The precipitation of tin as metastannic acid

$$3\,Sn + 4\,HNO_3 + xH_2O = 3\,SnO_2 \cdot xH_2O + 4\,NO$$

is not complete if the alloy contains much iron, say above 0.25 per cent.

[2] The metastannic acid that separates from solution is always contaminated by compounds of iron, copper, and zinc. If the alloy contains antimony, phosphorus, or arsenic these are also found in the precipitate, often quantitatively.

[3] In this treatment, which is essentially that used in Kjeldahl determinations, the paper and precipitate are transferred to a Kjeldahl flask, treated with 15 ml of H_2SO_4 and 5 g of Na_2SO_4, and then boiled gently until organic matter has been destroyed.

[4] In this treatment quadrivalent tin is reduced to the bivalent state

$$SnCl_4 + Pb + 2\,HCl = SnCl_2 + PbCl_2 + 2\,HCl.$$

The reducing action of the lead ceases as soon as the solution is cooled.

[5] In the titration with iodine the bivalent compound of tin is oxidized to the quadrivalent state

$$SnCl_2 + 2\,HCl + I_2 = SnCl_4 + 2\,HI.$$

Accompanying elements such as iron, copper, zinc, antimony, phosphorus, or arsenic are without effect.

[6] As stated in 1 and 2, some tin may be lost through incomplete precipitation, and the precipitate may be contaminated by iron, copper, zinc, antimony, phosphorus, or arsenic. In routine analyses of bronzes containing but moderate amounts of iron and no antimony, phosphorus, or arsenic, the extent of the errors can be determined, once and for all, by careful tests on similar bronzes of known composition, and fairly accurate corrections can be made. Corrections for the effects of the other elements are not safely made in this way, and other methods of analysis are generally used if they are present.

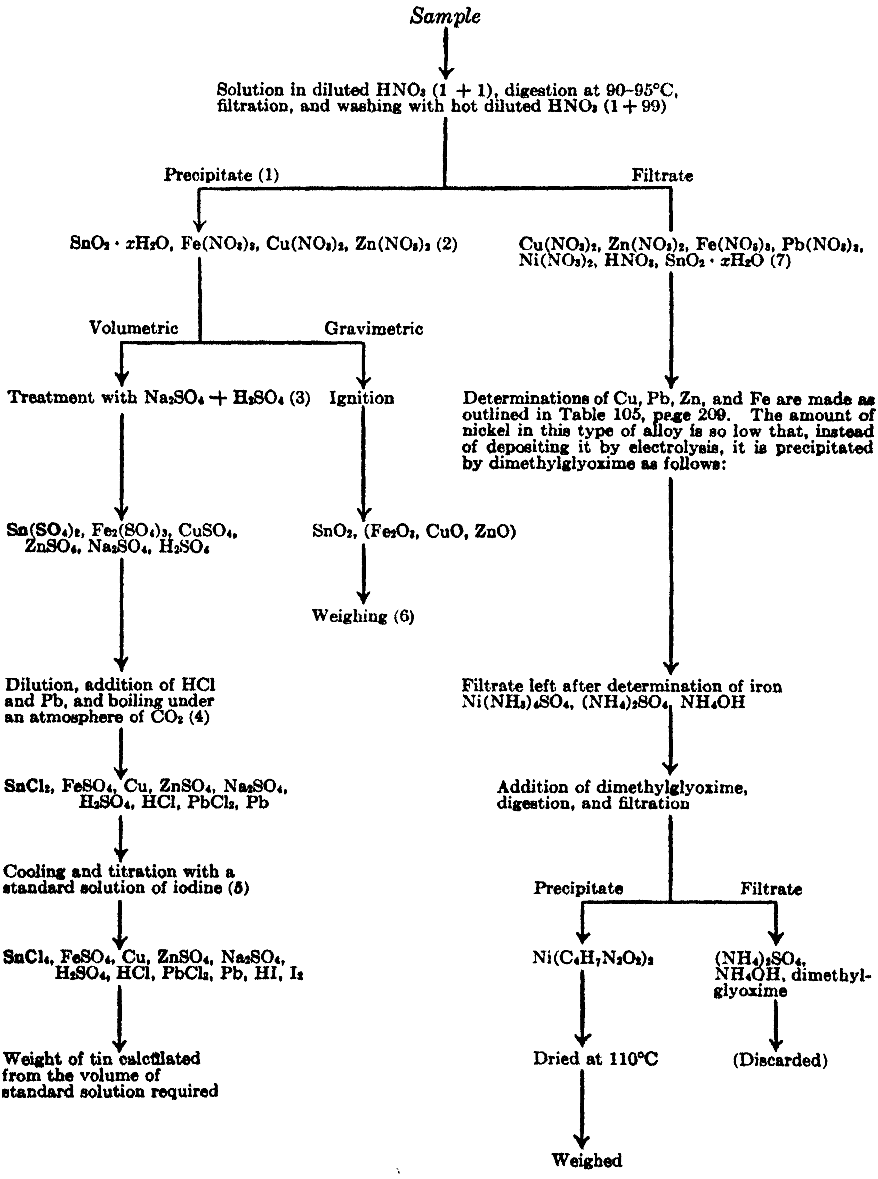
[7] Tin is an objectionable constituent in this filtrate. It leads to complications in the determination of copper, lead, and zinc because tin in the ionic state tends to contaminate the copper deposit, that present as colloidal metastannic acid tends to deposit with the lead, and any tin left in the electrolyte is precipitated with the zinc sulphide.

TABLE 106

Analysis of Bronze

(Cu, Sn, Zn, Pb, Fe, Ni)

A. Routine Analysis


Sample
Solution in diluted HNO_3 (1 + 1), digestion at 90–95°C, filtration, and washing with hot diluted HNO_3 (1 + 99)
Precipitate (1)
Filtrate
$SnO_2 \cdot xH_2O$, $Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ (2)
$Cu(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, $Pb(NO_3)_2$, $Ni(NO_3)_2$, HNO_3, $SnO_2 \cdot xH_2O$ (7)
Volumetric
Gravimetric
Treatment with Na_2SO_4 + H_2SO_4 (3)
Ignition
Determinations of Cu, Pb, Zn, and Fe are made as outlined in Table 105, page 209. The amount of nickel in this type of alloy is so low that, instead of depositing it by electrolysis, it is precipitated by dimethylglyoxime as follows:
$Sn(SO_4)_2$, $Fe_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$, Na_2SO_4, H_2SO_4
SnO_2, (Fe_2O_3, CuO, ZnO)
Weighing (6)
Dilution, addition of HCl and Pb, and boiling under an atmosphere of CO_2 (4)
Filtrate left after determination of iron $Ni(NH_3)_4SO_4$, $(NH_4)_2SO_4$, NH_4OH
$SnCl_2$, $FeSO_4$, Cu, $ZnSO_4$, Na_2SO_4, H_2SO_4, HCl, $PbCl_2$, Pb
Addition of dimethylglyoxime, digestion, and filtration
Cooling and titration with a standard solution of iodine (5)
Precipitate
Filtrate
$SnCl_4$, $FeSO_4$, Cu, $ZnSO_4$, Na_2SO_4, H_2SO_4, HCl, $PbCl_2$, Pb, HI, I_2
$Ni(C_4H_7N_2O_2)_2$
$(NH_4)_2SO_4$, NH_4OH, dimethylglyoxime
Weight of tin calculated from the volume of standard solution required
Dried at 110°C
(Discarded)
Weighed

B. Umpire Analysis

In umpire analyses of bronze, which must provide for all the sources of error, separate samples are usually taken for the determination of tin and for the determinations of the other elements. In one of these, as much metastannic acid is separated as possible, and the tin remaining in solution is recovered. The combined precipitates are dissolved, the tin is reduced to the bivalent state and then determined by oxidizing it to the quadrivalent state by means of a standard solution of iodine. In the second sample, the impurities in the metastannic acid are recovered and added to the nitric acid filtrate. From this point the analysis differs from that used in the analysis of German silver (see page 209) chiefly in that nickel is determined by precipitating with dimethylglyoxime (see page 211) instead of by electrodeposition. These treatments are illustrated in Table 107.

NOTES

[1] The treatment of the filtrate is usually unnecessary if the alloy contains little or no iron.

[2] As stated in 5 under " Routine Analysis," contaminants such as iron, copper, zinc, antimony, phosphorus, or arsenic are without effect in the iodimetric method for the determination of tin.

[3] It is very desirable that tin be completely removed at this point. If the composition of the alloy is such that the tin may not be completely precipitated by digestion with nitric acid, it is better to dissolve the sample in a mixture of nitric and hydrochloric acids, and to remove the tin by adding ammonium hydroxide in excess, boiling, filtering, and washing the precipitate. The recovery of copper, etc., in the precipitate and the determination of the elements are then made as outlined.

[4] In the most accurate work it is desirable to make sure of the removal of all tin by repeating the treatment with sodium hydroxide and sodium sulphide

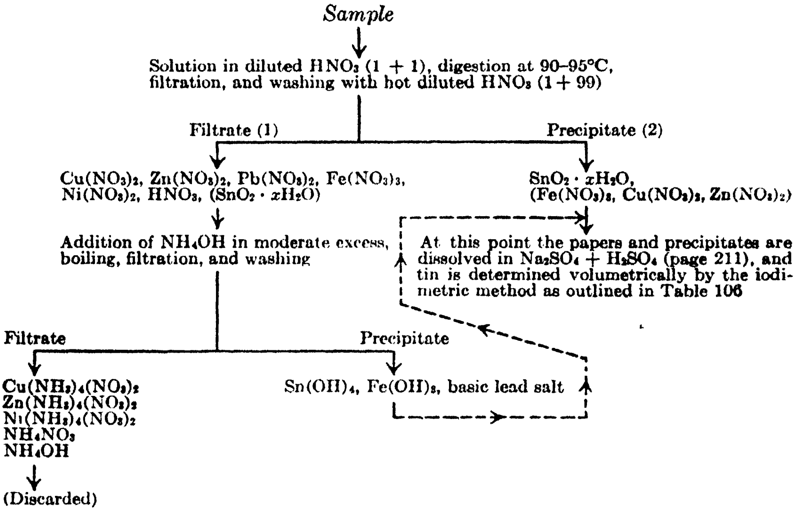
[5] To recover any copper or lead that may remain in the electrolyte after the electrodeposition of these constituents, it is well to treat it with hydrogen sulphide after its acidity has been reduced to about 0.3 N. If a precipitate appears, it is removed and examined for its lead and copper content, while the filtrate is boiled to expel hydrogen sulphide and the acidity reduced to 0.01 N before the zinc sulphide is precipitated.

TABLE 107

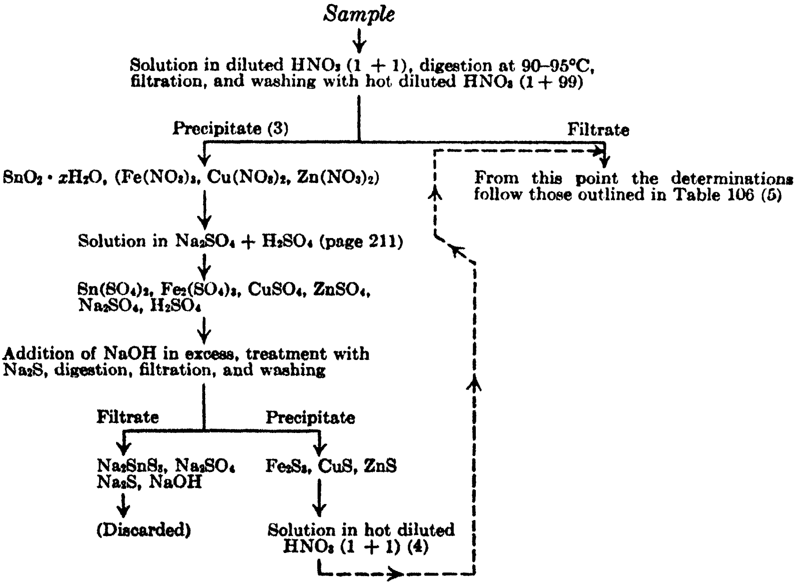
Analysis of Bronze (*continued*)

B. Umpire Analysis

I. DETERMINATION OF TIN ONLY


Sample
Solution in diluted HNO_3 (1 + 1), digestion at 90–95°C, filtration, and washing with hot diluted HNO_3 (1 + 99)
Filtrate (1)
Precipitate (2)
$Cu(NO_3)_2$, $Zn(NO_3)_2$, $Pb(NO_3)_2$, $Fe(NO_3)_3$, $Ni(NO_3)_2$, HNO_3, ($SnO_2 \cdot xH_2O$)
$SnO_2 \cdot xH_2O$, ($Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$)
Addition of NH_4OH in moderate excess, boiling, filtration, and washing
At this point the papers and precipitates are dissolved in Na_2SO_4 + H_2SO_4 (page 211), and tin is determined volumetrically by the iodimetric method as outlined in Table 106
Filtrate
Precipitate
$Cu(NH_3)_4(NO_3)_2$
$Zn(NH_3)_4(NO_3)_2$
$Ni(NH_3)_4(NO_3)_2$
NH_4NO_3
NH_4OH
(Discarded)
$Sn(OH)_4$, $Fe(OH)_3$, basic lead salt

II. DETERMINATIONS OF COPPER, LEAD, ZINC, IRON, AND NICKEL


Sample
Solution in diluted HNO_3 (1 + 1), digestion at 90–95°C, filtration, and washing with hot diluted HNO_3 (1 + 99)
Precipitate (3)
Filtrate
$SnO_2 \cdot xH_2O$, ($Fe(NO_3)_3$, $Cu(NO_3)_2$, $Zn(NO_3)_2$)
From this point the determinations follow those outlined in Table 106 (5)
Solution in Na_2SO_4 + H_2SO_4 (page 211)
$Sn(SO_4)_2$, $Fe_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$, Na_2SO_4, H_2SO_4
Addition of NaOH in excess, treatment with Na_2S, digestion, filtration, and washing
Filtrate
Precipitate
Na_2SnS_3, Na_2SO_4 Na_2S, NaOH
(Discarded)
Fe_2S_3, CuS, ZnS
Solution in hot diluted HNO_3 (1 + 1) (4)

CHAPTER LI

ANALYSIS OF PHOSPHOR BRONZE BEARING METAL

The following description applies to the analysis of an alloy which has a composition approximating that of the U. S. Bureau of Standards standard sample No. 63 of phosphor bronze bearing metal. In rounded off percentages, the composition of this alloy is Cu 78, Sn 9.9, Pb 9.7, P 0.6, Sb 0.6, Zn 0.5, Fe 0.3, As 0.2, S 0.06, Al 0.05, and Ni 0.01. In the analysis of such an alloy, tin, antimony, phosphorus, and arsenic are separated from the other elements by treating with diluted nitric acid and filtering as described under Bronze (page 210). Antimony and tin are then determined by (1) obtaining a sulphuric acid solution of the precipitate; (2) making sure that antimony and tin are in the trivalent and quadrivalent states, respectively; (3) oxidizing the antimony to the quinquevalent state by titrating with a standard solution of permanganate; (4) treating the titrated solution with lead in order to reduce the tin to the bivalent state; and (5) reoxidizing the tin to the quadrivalent state by titrating with a standard solution of iodine. Separate portions of sample are taken for determinations of phosphorus, sulphur, and arsenic. The remaining elements in the alloy are determined as in Bronze (page 210), except that lead is separated as sulphate because the amount is too large to determine by electrolysis, and the precipitate obtained with ammonium hydroxide must be examined for its alumina content.

The various steps of the analysis are shown in Tables 108–112.

NOTES

[1] With this type of alloy very little if any tin or antimony remains in solution at this point, and recoveries as described under Bronze are seldom worth while. In routine analyses this filtrate can be used for the determinations covered in Table 109.

[2] Usually the action of carbonaceous matter (from the filter paper) in the concentrated sulphuric acid solution serves to reduce antimony and arsenic to the trivalent state. Valences of the other elements are not changed.

[3] Titration with permanganate at this point causes oxidation of antimony from the trivalent to the quinquevalent state

$$5\ Sb_2(SO_4)_3 + H_2SO_4 + 4\ KMnO_4 + 24\ H_2O = 10\ H_3SbO_4 + 2\ K_2SO_4 + 4\ MnSO_4 + 10\ H_2SO_4.$$

Arsenic is oxidized as well, but never quite to the quinquevalent state. In ordinary analyses, the " apparent percentage " of antimony is calculated from the volume of permanganate required, and then corrected by subtracting 1.86 times the percentage of arsenic that is found by separate test as in (E). In analyses of the highest accuracy, arsenic is first removed, as for example by careful distillation of arsenic trichloride or by precipitation of the sulphide in strong hydrochloric acid solution.

[4] The percentage of tin is, of course, calculated from the volume of iodine solution required.

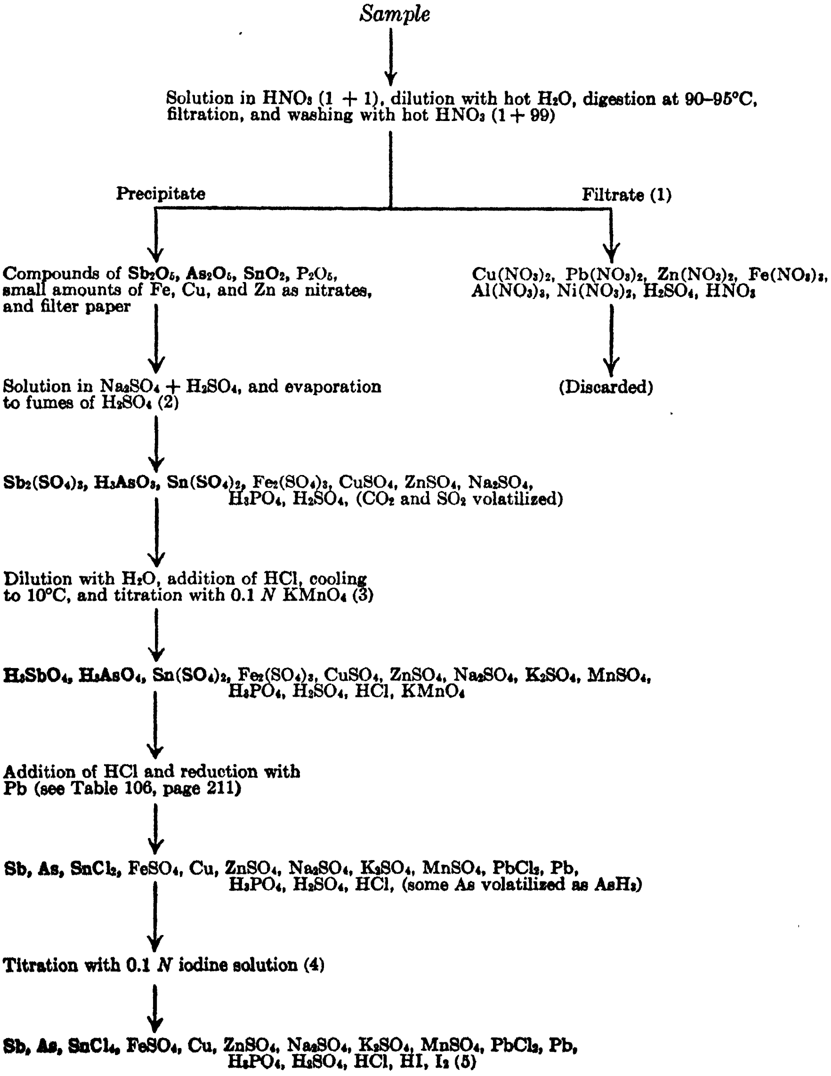
[5] It should be noted that the treatments following the separation of the nitric acid precipitate involve changes in the valences of ten elements (C, S, Sb, As, Mn, Sn, Fe, Cu, Pb, and I).

TABLE 108

Analysis of Phosphor Bronze Bearing Metal

(Cu, Sn, Pb, P, Sb, Zn, Fe, As, S, Al, Ni)

A. Determination of Antimony and Tin



Sample

Solution in HNO_3 (1 + 1), dilution with hot H_2O, digestion at 90–95°C, filtration, and washing with hot HNO_3 (1 + 99)

Precipitate

Compounds of Sb_2O_5, As_2O_5, SnO_2, P_2O_5, small amounts of Fe, Cu, and Zn as nitrates, and filter paper

Solution in Na_2SO_4 + H_2SO_4, and evaporation to fumes of H_2SO_4 (2)

$Sb_2(SO_4)_3$, H_3AsO_3, $Sn(SO_4)_2$, $Fe_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$, Na_2SO_4, H_3PO_4, H_2SO_4, (CO_2 and SO_2 volatilized)

Dilution with H_2O, addition of HCl, cooling to 10°C, and titration with 0.1 *N* $KMnO_4$ (3)

H_3SbO_4, H_3AsO_4, $Sn(SO_4)_2$, $Fe_2(SO_4)_3$, $CuSO_4$, $ZnSO_4$, Na_2SO_4, K_2SO_4, $MnSO_4$, H_3PO_4, H_2SO_4, HCl, $KMnO_4$

Addition of HCl and reduction with Pb (see Table 106, page 211)

Sb, As, $SnCl_2$, $FeSO_4$, Cu, $ZnSO_4$, Na_2SO_4, K_2SO_4, $MnSO_4$, $PbCl_2$, Pb, H_3PO_4, H_2SO_4, HCl, (some As volatilized as AsH_3)

Titration with 0.1 *N* iodine solution (4)

Sb, As, $SnCl_4$, $FeSO_4$, Cu, $ZnSO_4$, Na_2SO_4, K_2SO_4, $MnSO_4$, $PbCl_2$, Pb, H_3PO_4, H_2SO_4, HCl, HI, I_2 (5)

Filtrate (1)

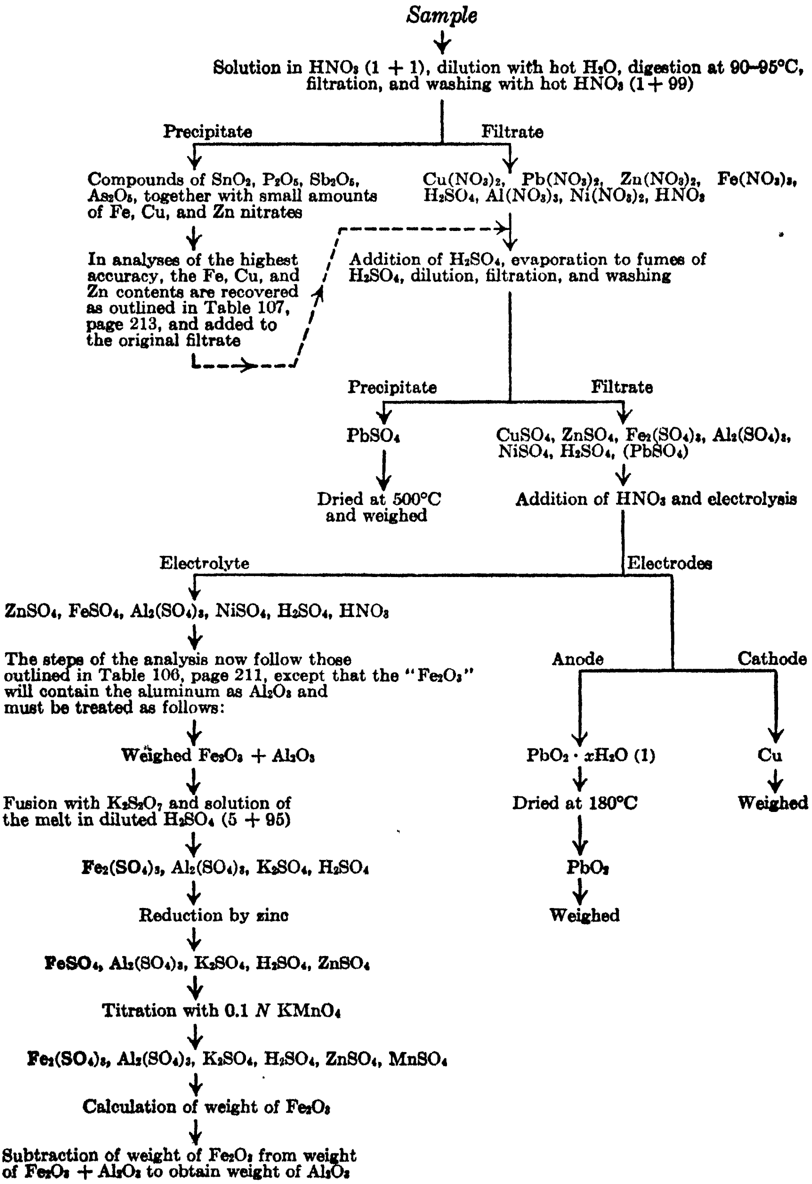
$Cu(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, $Al(NO_3)_3$, $Ni(NO_3)_2$, H_2SO_4, HNO_3

(Discarded)

TABLE 109

Analysis of Phosphor Bronze Bearing Metal (*continued*)

B. Determinations of Copper, Lead, Zinc, Iron, Aluminum, and Nickel


Sample
Solution in HNO_3 (1 + 1), dilution with hot H_2O, digestion at 90–95°C, filtration, and washing with hot HNO_3 (1 + 99)
Precipitate
Filtrate
Compounds of SnO_2, P_2O_5, Sb_2O_5, As_2O_5, together with small amounts of Fe, Cu, and Zn nitrates
$Cu(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, H_2SO_4, $Al(NO_3)_3$, $Ni(NO_3)_2$, HNO_3
In analyses of the highest accuracy, the Fe, Cu, and Zn contents are recovered as outlined in Table 107, page 213, and added to the original filtrate
Addition of H_2SO_4, evaporation to fumes of H_2SO_4, dilution, filtration, and washing
Precipitate
Filtrate
$PbSO_4$
Dried at 500°C and weighed
$CuSO_4$, $ZnSO_4$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $NiSO_4$, H_2SO_4, ($PbSO_4$)
Addition of HNO_3 and electrolysis
Electrolyte
Electrodes
$ZnSO_4$, $FeSO_4$, $Al_2(SO_4)_3$, $NiSO_4$, H_2SO_4, HNO_3
The steps of the analysis now follow those outlined in Table 106, page 211, except that the "Fe_2O_3" will contain the aluminum as Al_2O_3 and must be treated as follows:
Weighed Fe_2O_3 + Al_2O_3
Fusion with $K_2S_2O_7$ and solution of the melt in diluted H_2SO_4 (5 + 95)
$Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, K_2SO_4, H_2SO_4
Reduction by zinc
$FeSO_4$, $Al_2(SO_4)_3$, K_2SO_4, H_2SO_4, $ZnSO_4$
Titration with 0.1 *N* $KMnO_4$
$Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, K_2SO_4, H_2SO_4, $ZnSO_4$, $MnSO_4$
Calculation of weight of Fe_2O_3
Subtraction of weight of Fe_2O_3 from weight of Fe_2O_3 + Al_2O_3 to obtain weight of Al_2O_3
Anode
Cathode
$PbO_2 \cdot xH_2O$ (1)
Dried at 180°C
PbO_2
Weighed
Cu
Weighed

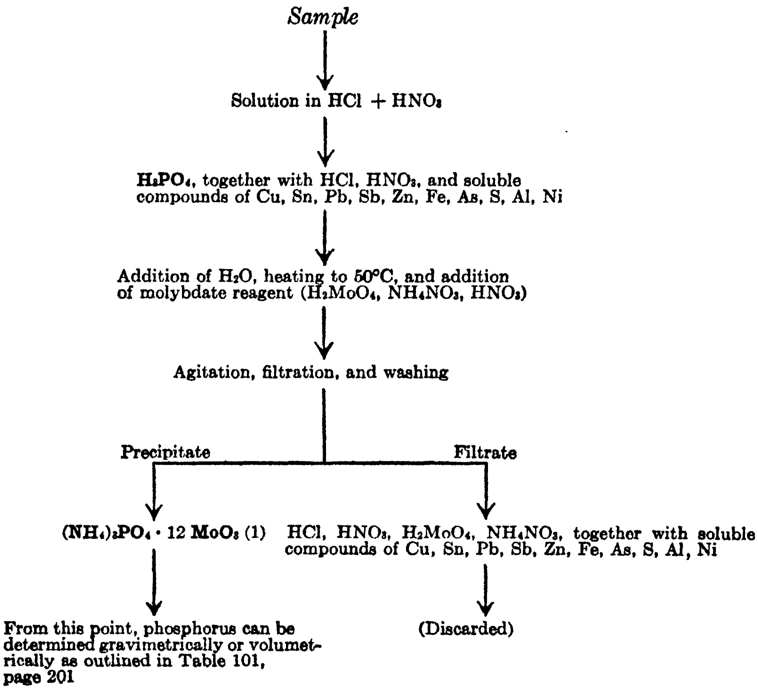
---

[1] If any lead has escaped precipitation as the sulphate, it forms the characteristic brown deposit of hydrated lead dioxide on the anode and can be weighed as PbO_2.

TABLE 110

Analysis of Phosphor Bronze Bearing Metal *(continued)*

C. Determination of Phosphorus


Sample
Solution in HCl + HNO_3
H_3PO_4, together with HCl, HNO_3, and soluble compounds of Cu, Sn, Pb, Sb, Zn, Fe, As, S, Al, Ni
Addition of H_2O, heating to 50°C, and addition of molybdate reagent (H_2MoO_4, NH_4NO_3, HNO_3)
Agitation, filtration, and washing
Precipitate
Filtrate
$(NH_4)_3PO_4 \cdot 12\ MoO_3$ (1)
HCl, HNO_3, H_2MoO_4, NH_4NO_3, together with soluble compounds of Cu, Sn, Pb, Sb, Zn, Fe, As, S, Al, Ni
From this point, phosphorus can be determined gravimetrically or volumetrically as outlined in Table 101, page 201
(Discarded)

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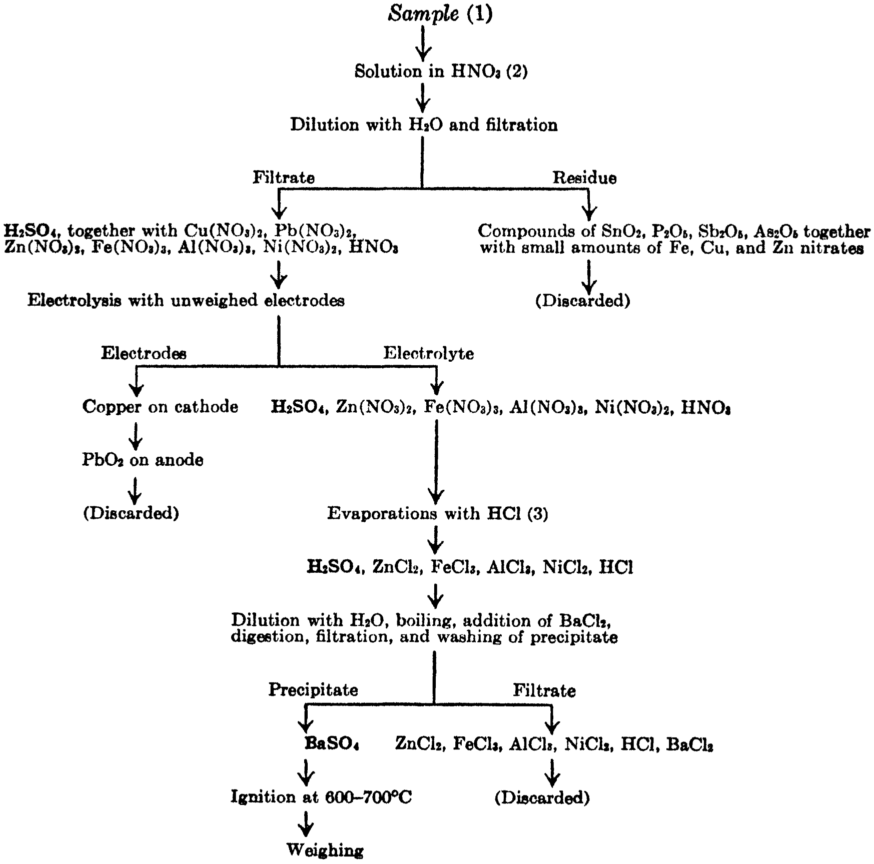
[1] The precipitate contains little or no arsenic if conditions are established so that the temperature of the solution does not exceed 40°C after the molybdate reagent has been added.

TABLE 111

Analysis of Phosphor Bronze Bearing Metal (*continued*)

D. Determination of Sulphur


Sample (1)
Solution in HNO_3 (2)
Dilution with H_2O and filtration
Filtrate
Residue
H_2SO_4, together with $Cu(NO_3)_2$, $Pb(NO_3)_2$, $Zn(NO_3)_2$, $Fe(NO_3)_3$, $Al(NO_3)_3$, $Ni(NO_3)_2$, HNO_3
Compounds of SnO_2, P_2O_5, Sb_2O_5, As_2O_5 together with small amounts of Fe, Cu, and Zn nitrates
Electrolysis with unweighed electrodes
(Discarded)
Electrodes
Electrolyte
Copper on cathode
H_2SO_4, $Zn(NO_3)_2$, $Fe(NO_3)_3$, $Al(NO_3)_3$, $Ni(NO_3)_2$, HNO_3
PbO_2 on anode
(Discarded)
Evaporations with HCl (3)
H_2SO_4, $ZnCl_2$, $FeCl_3$, $AlCl_3$, $NiCl_2$, HCl
Dilution with H_2O, boiling, addition of $BaCl_2$, digestion, filtration, and washing of precipitate
Precipitate
Filtrate
$BaSO_4$
$ZnCl_2$, $FeCl_3$, $AlCl_3$, $NiCl_3$, HCl, $BaCl_2$
Ignition at 600–700°C
(Discarded)
Weighing

NOTES

[1] Five 1-g samples are usually carried along separately, and the solutions are combined after the electrolytes have been evaporated to small volume. This is done because it is difficult to carry along from the start the 5-g sample needed to insure moderate accuracy in the determination of this low-percentage constituent.

[2] Concentrated nitric acid is used at this point in order to insure the oxidation of the "sulphide" sulphur to sulphuric acid

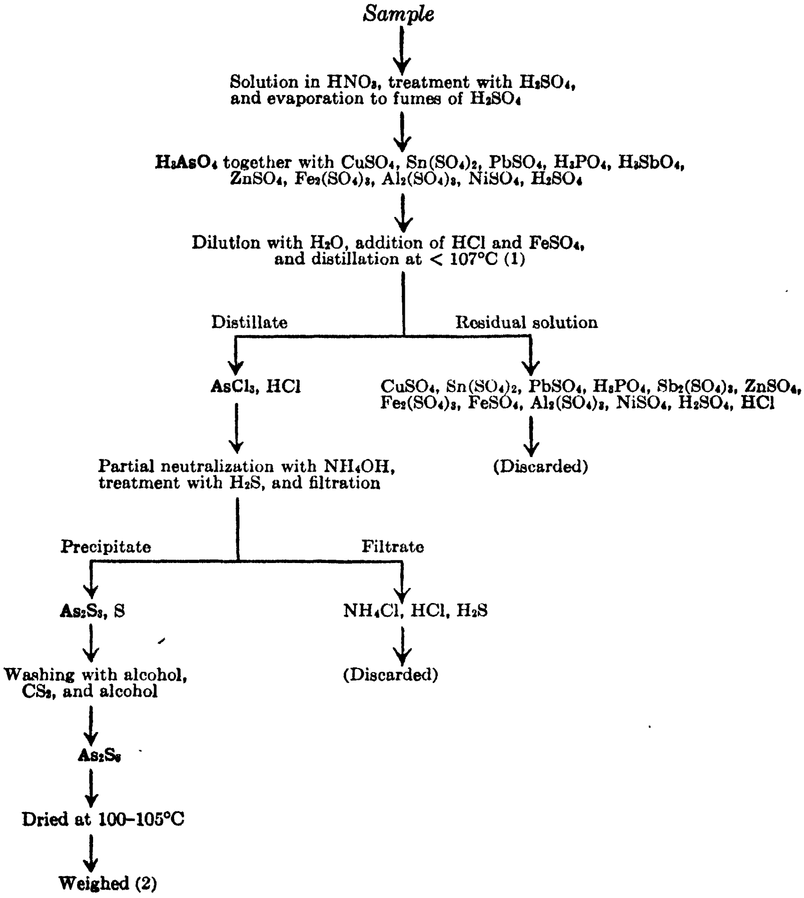
$$3\,CuS + 14\,HNO_3 = 3\,Cu(NO_3)_2 + 3\,H_2SO_4 + 8\,NO + 4\,H_2O.$$

[3] Evaporations with hydrochloric acid are made in order to expel nitric acid and nitrates, which might otherwise cause precipitation of the sparingly soluble barium nitrate.

TABLE 112

Analysis of Phosphor Bronze Bearing Metal (*continued*)

E. Determination of Arsenic


Sample
Solution in HNO_3, treatment with H_2SO_4, and evaporation to fumes of H_2SO_4
H_3AsO_4 together with $CuSO_4$, $Sn(SO_4)_2$, $PbSO_4$, H_3PO_4, H_3SbO_4, $ZnSO_4$, $Fe_2(SO_4)_3$, $Al_2(SO_4)_3$, $NiSO_4$, H_2SO_4
Dilution with H_2O, addition of HCl and $FeSO_4$, and distillation at < 107°C (1)
Distillate
Residual solution
$AsCl_3$, HCl
$CuSO_4$, $Sn(SO_4)_2$, $PbSO_4$, H_3PO_4, $Sb_2(SO_4)_3$, $ZnSO_4$, $Fe_2(SO_4)_3$, $FeSO_4$, $Al_2(SO_4)_3$, $NiSO_4$, H_2SO_4, HCl
Partial neutralization with NH_4OH, treatment with H_2S, and filtration
(Discarded)
Precipitate
Filtrate
As_2S_3, S
NH_4Cl, HCl, H_2S
Washing with alcohol, CS_2, and alcohol
(Discarded)
As_2S_3
Dried at 100–105°C
Weighed (2)

NOTES

[1] If the temperature of the vapor is allowed to rise above 107°C, more or less antimony accompanies arsenic and is later also precipitated as sulphide, thus causing high results for arsenic.

[2] Arsenic can also be determined by neutralizing the hydrochloric acid distillate (with NaOH at first and $NaHCO_3$ at the end) and titrating with a standard solution of iodine; or by converting the arsenious sulphide to silver arsenate; dissolving this in nitric acid, titrating the silver by the Volhard method, and calculating the amount of arsenic from the ratio 1 As = 3 Ag. The latter modification can be applied even though moderate amounts of antimony have passed into the distillate.

PART V. EVALUATION OF RESULTS, AND STANDARD ANALYZED SAMPLES

CHAPTER LII

EVALUATION OF RESULTS OBTAINED IN CHEMICAL ANALYSES

A. Accuracy and Precision of Results

The analyst should form the habit of estimating the probable accuracy of his work. It is a common mistake to confuse precision with accuracy. Accuracy is a measure of the degree of correctness. Precision is a measure of reproducibility in the hands of a given operator. The precision of a result does not necessarily have anything to do with its accuracy. Each of a dozen analysts may obtain exactly the same result in a given analysis (precision), and yet that result may be 100 per cent in error (accuracy). The causes for discrepancies between precision and accuracy are not difficult to find. For example, both titanium and aluminum are precipitated by ammonium hydroxide and converted to stable oxides upon ignition. If, then, the analyst is dealing with an unknown material containing equal amounts of the oxides of the two elements, he may obtain perfect checks in a whole series of results obtained by precipitating with ammonium hydroxide, igniting the precipitate, and weighing the residue. This would indicate a very high precision, and yet, if he fails to discover the presence of titanium and proceeds to calculate on the assumption that aluminum is the only element present, he will not only fail to report titanium but he will also make a 100 per cent error in his report for alumina.

A reported result should not imply an accuracy that is much greater than can be obtained by the method used. If, for example, 0.0100 g of alumina is obtained in a gravimetric determination of aluminum in a 1-g sample, and this is multiplied by the factor for aluminum in alumina (0.5291), the product is 0.005291. The question then is whether the percentage of aluminum should be reported as 0.5291, 0.529, 0.53, or 0.5. As a first consideration, the reported result should not exceed that warranted by the method of weighing. The ordinary analytical balance is not sensitive to a mass lighter than one-twentieth of a milligram. So far as the balance was concerned the weight of alumina might therefore have been 0.01005 or 0.00995, and the percentage of alumina 0.5317 or 0.5265. The analyst would therefore have no justification for choosing 0.5291 as against 0.5265 or 0.5317 and had better report 0.529 and indicate the uncertainty as ±0.003. Stated in another way, an error of 0.05 mg in the weighing of 0.0100 g represents an error of 5 parts in 1000 or 1 part in 200, and the significant figures in the reported result should not imply much greater accuracy than this. Since other sources of error may exist, the rounded value 0.53 is probably all that can be justified.

Similar considerations hold in volumetric analyses. The smallest subdivision on an ordinary burette represents 0.1 ml. In determining the volume of a solution that has been delivered by such a burette, the analyst can easily make an error of 0.01 ml in both initial and final readings, or an error of 0.02 ml in the recorded volume. So far as the reading of the volume is concerned, a recorded volume of 26.15 ml might just as well be 26.17 or 26.13. If the volume is that of a permanganate solution which represents 0.0056 g of iron per milliliter and has been needed to oxidize the iron obtained from 0.25 g of iron ore, the percentage of iron may lie anywhere between 58.531 and 58.621. A report of 58.576, based on the volume 26.15, is therefore unjustified and misleading as to the probable accuracy of the determination. If only one determination has been made, the analyst had better indicate his uncertainty by reporting 58.6. If the result 58.576 is the average of a number of determinations that agree closely, a rounded-off figure of 58.58 may be justified. In this case, the result had better be written 58.5_8 which indicates that the analyst believes the ore to contain at least 58.5 per cent of the constituent, and that the true percentage of iron may lie between 58.575 and 58.584.

Determinations are subject to many errors besides those made in weighing or measuring. Some analyses involve a dozen or more operations, in each of which an error may be made. Some of these errors are largely avoidable, as for example those incurred in transferring the sample to the reaction vessel, obtaining the solution of the sample, transferring solutions or precipitates, and igniting precipitates. On the other hand, certain errors may be inherent in methods of analysis, as for example those caused by imperfect separations, solubility of precipitates, or uncertain composition of the final products.

In reporting results, special work is usually required to justify more than three significant figures for percentages involving whole numbers, and two significant figures for percentages involving decimal fractions only, as for example percentages of 68.3 for iron in an iron ore, 1.26 for silicon in cast iron, 0.56 for alumina in glass, or 0.023 for titania in a rock.

B. Evaluation of Results Obtained in Repeated Determinations by a Single Analyst

Arithmetical Mean. Elaborate mathematical treatments of an analyst's results are seldom of much value unless at least five results are available. In ordinary analyses of a given material the analyst seldom makes enough determinations of a given constituent by a given method to warrant any mathematical treatment of the results other than the taking of their arithmetical mean. This is obtained by adding all the results, $a_1, a_2 \dots a_n$, that have an equal degree of probability, and then dividing by the number of determinations:

$$\text{Arithmetical mean} = \frac{\text{Sum of results}}{\text{Number of determinations}}, \text{ or } M = \frac{\sum a}{n}.$$

This may be called the best representative value of the series of results. If enough determinations have been carefully made by the analyst, it is evident that this value is the best that he can expect to obtain under the circumstances. It should be emphasized that it does not necessarily represent the *true* value, for the chemical method may be subject to constant unsuspected errors.

Deviation from the Mean. The difference, d, between the result obtained in any determination in the series and the arithmetical mean of the series is the deviation of that result from the mean. Deviations may be plus or minus, as the results are greater or less than the mean. In the succeeding discussion the magnitude and not the direction of the deviation is of moment.

Average Deviation from the Mean. The average deviation from the mean is obtained by computing the numerical deviations, $d_1, d_2, \dots d_n$, of a series of determinations, adding these without regard to sign, and dividing by the number of determinations:

$$\text{Average deviation} = \frac{\text{Sum of deviations from the mean}}{\text{Number of determinations}}, \text{ or } AD = \frac{\sum d}{n}.$$

Rejection of Results. Occasionally, in a series of four or more results obtained under apparently identical conditions one result differs so much from the others that there is a temptation to reject it. This may be done if the discrepancy can be traced to an obvious mistake, such as recording the wrong weight, mechanical loss of material, or the like. If no such obvious mistake can be found, a good criterion is the following: compute the mean and the average deviation, omitting the doubtful result. Then compute the deviation of the doubtful result from the mean. If this is equal to, or greater than, four times the average deviation, the result can be rejected, for it can be shown that the probability of the occurrence of a result with a deviation as large as this is only about 1 in 1000.

Probable Error. The probable error (probable deviation) of a single determination is a measure of the *precision* of the method. It does *not* refer to the *accuracy* of the method or the magnitude of the actual error. If two or more determinations have been made, the probable error of a single determination can be calculated by making use of the principle of least squares, according to which the best value of observed quantities having an equal degree of probability is that which makes the sum of the squares of their deviation from the mean a minimum. This can be expressed by

$$\text{Probable error of a single determination} = 0.6745\sqrt{\frac{\Sigma(d^2)}{n-1}}.$$

The smaller the value, the more precise the method, for in each determination the chance of obtaining a result having a deviation greater than the probable error is equal to the chance of obtaining a result less than it.

The probable error of the arithmetical mean of a whole series of determinations is expressed by

$$\text{Probable error of the mean} = 0.6745\sqrt{\frac{\Sigma(d^2)}{n(n-1)}}$$

and reflects the increase in the reliability of the mean that can be expected by increasing the number of determinations. In both calculations $\frac{2}{3}$ is usually substituted for 0.6745.

What has been said pertains chiefly to that type of error which may be termed accidental. A small average deviation, or a small probable error in a chemical determination, can be interpreted only as a measure of the precision with which the results were obtained. Favorable figures for these do not necessarily mean that results are accurate. In fact, their probable accuracy cannot be established by mathematical treatment alone, for residual errors, that is, errors inherent in the chemical methods themselves, can be determined only by observation and experience. The most scrupulous mathematical treatment of 50 closely checking results obtained by the use of a faulty chemical method will not give a value that is as reliable as one obtained by taking the simple arithmetical mean of three or four results obtained by a well-planned and well-manipulated chemical method.

C. Evaluation of Results Obtained by Two or More Analysts

Occasionally it becomes important to evaluate and correlate the results obtained by a number of analysts who have followed the same method to the best of their ability, or even different methods, provided all obvious errors inherent in the methods have been eliminated. For this purpose it is desirable to employ a more reasonable or conservative estimate of the uncertainty in each analyst's result than is furnished by the probable error. If the individual results are available, the probable error of each analyst's averaged result should be calculated and then some reasonable multiple of it taken as the expression of the uncertainty in the result. No fixed multiple of the probable error is universally employed, but 3 and 5 are used quite often. If the multiple 3 is used, the limits will be such that the best representative value has a chance of 22 to 1 of falling within them. In the discussion that follows, three times the calculated probable error is used to denote the reasonable uncertainty in each averaged result. This is then added to, and subtracted from, the averaged result to obtain the reasonable limits represented by the result. Results so treated are regarded as consistent if they show at least one common value within their reasonable limits.

This may be illustrated in Table 113, in which the results reported by

TABLE 113

Results for Iron in Iron Ore Reported by Two Analysts

Analyst	Percentages of Iron Found		Arithmetical Mean	Average Deviation	Probable Error of a Single Determination	Probable Error of the Mean	Reasonable Limit of the Mean
	68.24		......	......	......	......	......
1	68.26		68.29	0.04	0.032	0.016	0.048
	68.32		......	......	......	......	......
	68.34		......	......	......	......	......
	68.19	68.25	......	......	......	......	......
	68.20	68.25	......	......	......	......	......
2	68.20	68.26	68.23	0.027	0.02	0.007	0.02
	68.21	68.27	......	......	......	......	......
	68.24	.....	......	......	......	......	......

two analysts for the percentage of iron in an iron ore are tabulated, and the quantities under discussion have been calculated. The two results 68.23 and 68.29 are consistent because the reasonable limits 68.21–68.25 and 68.242–68.338 agree in the range 68.242–68.25. If a third analyst reported the result 68.35 with a reasonable limit of 0.04 (68.31–68.39) it is consistent with the result 68.29 (68.242–68.338) because they agree in the range 68.31–68.338. It is not consistent with the result 68.23 because their reasonable limits contain no common value. Such a condition calls for a search for errors inherent in the methods.

The data also indicate that, if the first analyst repeated his determination by the same method, half of the means of two or more series of results could be expected to fall within 0.016 of 68.29 and half of the individual results could be expected to fall within 0.032 of 68.29.

The reasonable limit obtained by multiplying the probable error by 3 gives a simple conservative means of expressing the plus and minus limits to be used in reporting results. Other methods[1] of arriving at this are in use, but for the treatment of results obtained in chemical analysis such a method should be as simple as possible. By this procedure it would be reasonable to report the result obtained by the first analyst in Table 113 as 68.29 ± 0.05 (0.048 rounded to 0.05) and that obtained by the second analyst as 68.23 ± 0.02.

An illustration will show the relative uselessness of making a very large number of determinations. If 16 determinations had been made by the first analyst and deviations had remained the same, the probable error of the mean would have been $\frac{2}{3}\sqrt{\frac{0.0272}{16(15)}} = 0.007$. That is, quadrupling the number of determinations would have been required to cut the probable error approximately in half.

D. The Weighted Mean

Frequently it is necessary to evaluate a series of results which have not been obtained under like conditions and which are therefore not equally probable. Results obtained by two chemical methods or by two analysts of unequal reliability should not be averaged without due consideration of the merits of the methods or the analysts. In such case, results are usually weighted inversely as the squares of their probable errors. Thus, in the absence of any other information, if a final average between the results reported by the two analysts in Table 113 is to be obtained, the results of the first, with a probable error of 0.016, would receive only about $\frac{1}{5}$ the weight given to that of the second with a probable error of 0.007. Supplementary information may, however, justify assigning to averaged results weights other than those given by the inverse square rule. Weighting may be done in various ways, but the results obtained lose much of their value unless the method of weighting is designated.

In averaging a series of results, the circumstances under which the individual values were obtained may have a bearing on the weights to be assigned. For example, results obtained by the use of small samples are not as reliable as those obtained with samples of proper weight in a series of determinations in macro analysis. Under such circumstances the simple arithmetical mean is less reliable than a weighted mean obtained by giving added importance to the results known to be more reliable. This can be illustrated by the data following:

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[1] See Report of Committee on Manual on Presentation of Data, Proceedings of A.S.T.M., Vol. 33, Appendix, p. 451 (1933), and Vol. 35, Part I (1935).

Weight of acid potassium phthalate	Volume of 0.15 N NaOH	
	Required	Equivalent to 1 g of phthalate
g	ml	ml
0.2500	8.16	32.64
0.2500	8.15	32.60
0.5000	16.29	32.58
1.0000	32.53	32.53
1.0000	32.53	32.53
	Arithmetical Mean =	32.58

In these titrations added importance should be given the results obtained with the larger samples by dividing the total volume of alkali (97.66 ml) by the total weight of phthalate (3 g) to obtain the weighted average 32.55.

In weighting results by any method, good judgment is paramount in the selection of the proper " weights " and the method of applying them.

CHAPTER LIII

STANDARD ANALYZED SAMPLES

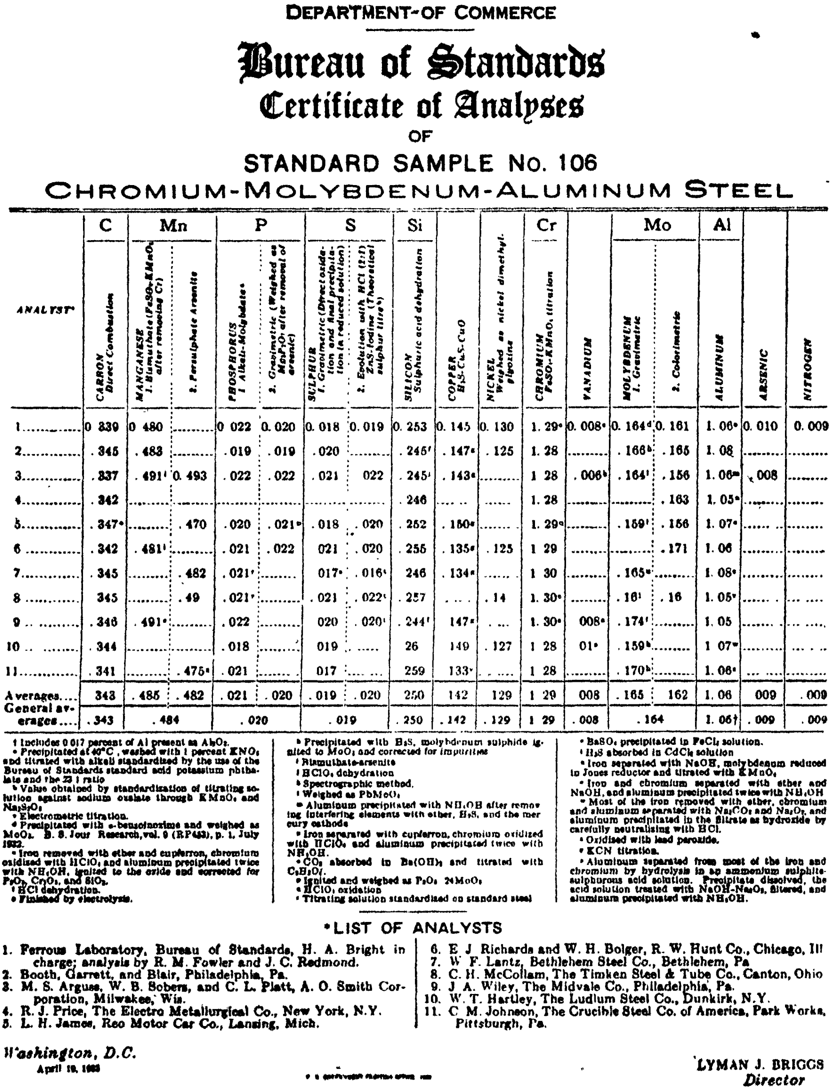
It has been shown that the factors that may affect the results of analytical determinations are many. When the technical chemist is called upon to devise new and rapid methods to fit complex materials of a hitherto uninvestigated nature, he cannot generally avail himself of the methods of the research chemist who can investigate one or two variables at a time. The time at his disposal is necessarily limited, and work must be conducted along lines of greatest efficiency. One result of this has been the evolution of standard analyzed materials. These may be defined as homogeneous materials resembling as closely as possible in chemical and physical nature the materials with which the chemist expects to deal, and which have been analyzed by a sufficient number of methods and analysts to establish their composition with considerable certainty. A typical certificate of analyses is shown in Table 114.

The advantage of a standard sample is that it behaves like the unknown material which the chemist intends to analyze, and consequently errors arising from factors such as solubility of precipitates, varying concentrations, and effects of one element upon the precipitation of another will affect both sample and standard alike. Hence, if standard and sample are analyzed at the same time (and under practically identical conditions) and results are obtained for the standard corresponding to those that are certified, the presumption is strong that the values obtained for the unknown material are equally accurate, whereas wide divergence from the certificate results shows at once that something is radically wrong, such as improper methods, faulty manipulation, or impure reagents. Thus, in the simplest possible manner and in the shortest possible time, a large number of variable factors can be simultaneously investigated with almost the same result as though each had been taken up separately.

Theoretically, there should be provided for the analyst as many standard samples as he has different kinds of materials to analyze. Such a program would require thousands of samples and is quite out of the question. Standards which cover important groups of materials have been prepared, notably by the National Bureau of Standards. A list of the samples that are distributed by this Bureau is given in Table 115. It will be noted that a few samples are certified for their physical rather than their chemical properties.

TABLE 114

Typical Certificate of Analyses Furnished with the Standard Samples Issued by the National Bureau of Standards



DEPARTMENT OF COMMERCE

Bureau of Standards

Certificate of Analyses

OF

STANDARD SAMPLE No. 106

CHROMIUM-MOLYBDENUM-ALUMINUM STEEL

	C	Mn		P		S		Si			Cr		Mo		Al		
ANALYST[*]	*CARBON Direct Combustion*	*MANGANESE 1. Bismuthate ($FeSO_4$-$KMnO_4$ after removing Cr)*	*2. Persulphate Arsenite*	*PHOSPHORUS 1 Alkali-Molybdate*	*2. Gravimetric (Weighed as $Mg_2P_2O_7$ after removal of arsenic)*	*SULPHUR 1. Gravimetric (Direct oxidation and final precipitation in reduced solution)*	*2. Evolution with HCl (1:1) ZnS-Iodine (Theoretical sulphur titre[t])*	*SILICON Sulphuric acid dehydration*	*COPPER H_2S-CuS-CuO*	*NICKEL Weighed as nickel dimethylglyoxime*	*CHROMIUM $FeSO_4$-$KMnO_4$ titration*	*VANADIUM*	*MOLYBDENUM 1. Gravimetric*	*2. Colorimetric*	*ALUMINUM*	*ARSENIC*	*NITROGEN*
1	0 339	0 480	....	0 022	0.020	0.018	0.019	0.253	0.145	0.130	1.29[q]	0.008[c]	0.164[d]	0.161	1.06[e]	0.010	0.009
2	.345	.483	....	.019	.019	.020	....	.245[f]	.147[g]	.125	1.28	....	.166[h]	.165	1.08	....	....
3	.337	.491[i]	0.493	.022	.022	.021	022	.245[j]	.143[g]	....	1 28	.006[k]	.164[l]	.156	1.06[m]	.008	....
4	.342	....	....	....	....	....	....	.246	......	......	1.28	....	....	.163	1.05[n]	....	....
5	.347[o]	....	.470	.020	.021[p]	.018	.020	.252	.150[g]	....	1.29[q]	....	.159[l]	.156	1.07[e]	....	....
6	.342	.481[i]	....	.021	.022	021	.020	.255	.135[g]	.125	1 29	....	....	.171	1.06	....	....
7	.345	....	.482	.021[r]	....	017[s]	.016[t]	246	.134[g]	......	1 30	....	.165[u]	....	1.08[e]	....	....
8	345	....	.49	.021[r]	....	.021	.022[t]	.257	....	.14	1.30[x]	....	.16[l]	.16	1.05[v]	....	....
9	.346	.491[c]	....	.022	....	020	.020[t]	.244[f]	147[g]	....	1.30[x]	008[x]	.174[u]	....	1.05	....	....
10	.344	....	....	.018	....	019	......	26	149	.127	1 28	01[x]	.159[h]	....	1 07[w]	....	....
11	.341	....	.475[c]	.021	....	017	......	259	133[y]	......	1 28	....	.170[h]	....	1.06[z]	....	....
Averages	343	.485	.482	.021	.020	.019	.020	250	142	129	1 29	008	.165	162	1.06	009	.009
General averages	.343	.484		.020		.019		.250	.142	.129	1 29	.008	.164		1.06†	.009	.009

† Includes 0.017 percent of Al present as Al_2O_3.

[a] *Precipitated at 40°C, washed with 1 percent KNO_3 and titrated with alkali standardized by the use of the Bureau of Standards standard acid potassium phthalate and the 23:1 ratio*

[b] Value obtained by standardization of titrating solution against sodium oxalate through $KMnO_4$ and $Na_2S_2O_3$

[c] Electrometric titration.

[d] Precipitated with α-benzoinoxime and weighed as MoO_3. B. S. Jour Research, vol. 9 (RP483), p. 1, July 1932.

[e] Iron removed with ether and cupferron, chromium oxidized with $HClO_4$ and aluminum precipitated twice with NH_4OH, ignited to the oxide and corrected for P_2O_5, Cr_2O_3, and SiO_2.

[f] HCl dehydration.

[g] *Finished by electrolysis.*

[h] Precipitated with H_2S, molybdenum sulphide ignited to MoO_3 and *corrected for impurities*

[i] Bismuthate-arsenite

[j] $HClO_4$ dehydration

[k] Spectrographic method.

[l] Weighed as $PbMoO_4$

[m] Aluminum precipitated with NH_4OH after removing interfering elements with ether, H_2S, and the mercury cathode

[n] Iron separated with cupferron, chromium oxidized with $HClO_4$ and aluminum precipitated twice with NH_4OH.

[o] CO_2 absorbed in $Ba(OH)_2$ and titrated with $C_2H_2O_4$.

[p] Ignited and weighed as $P_2O_5 \cdot 24MoO_3$

[q] $HClO_4$ oxidation

[r] Titrating solution standardized on standard steel

[s] $BaSO_4$ precipitated in $FeCl_3$ solution.

[t] H_2S absorbed in $CdCl_2$ solution

[u] Iron separated with NaOH, molybdenum reduced in Jones reductor and titrated with $KMnO_4$

[v] Iron and chromium separated with ether and NaOH, and aluminum precipitated twice with NH_4OH

[w] Most of the iron removed with ether, chromium and aluminum separated with Na_2CO_3 and Na_2O_2, and aluminum precipitated in the filtrate as hydroxide by carefully neutralizing with HCl.

[x] Oxidised with lead peroxide.

[y] KCN titration.

[z] Aluminum separated from most of the iron and chromium by hydrolysis in an ammonium sulphite-sulphurous acid solution. Precipitate dissolved, the acid solution treated with $NaOH$-Na_2O_2, filtered, and aluminum precipitated with NH_4OH.

[*]LIST OF ANALYSTS

1. Ferrous Laboratory, Bureau of Standards, H. A. Bright in charge; *analysis by R. M. Fowler and J. C. Redmond.*
2. Booth, Garrett, and Blair, Philadelphia, Pa.
3. M. S. Arguss, W. B. Sobers, and C. L. Platt, A. O. Smith Corporation, Milwakee, Wis.
4. R. J. Price, The Electro Metallurgical Co., New York, N.Y.
5. L. H. James, Reo Motor Car Co., Lansing, Mich.
6. E J Richards and W. H. Bolger, R. W. Hunt Co., Chicago, Ill
7. W F. Lantz, Bethlehem Steel Co., Bethlehem, Pa
8. C. H. McCollam, The Timken Steel & Tube Co., Canton, Ohio
9. J A. Wiley, The Midvale Co., Philadelphia, Pa.
10. W. T. Hartley, The Ludlum Steel Co., Dunkirk, N.Y.
11. C M. Johnson, The Crucible Steel Co. of America, Park Works, Pittsburgh, Pa.

Washington, D.C.
April 19, 1933

[illegible]

LYMAN J. BRIGGS
Director

Full information concerning the values that are certified, the weights and prices of the standards, and the procedure to be followed in purchasing the samples is contained in the Supplement to the National Bureau of Standards Circular C 398, which can be obtained free of charge upon application to the National Bureau of Standards, Washington, D. C.

TABLE 115

Standard Samples Issued by the National Bureau of Standards

Steels

Sample Number	Name	Constituents Determined or Intended Use
8e	Bessemer, 0.1 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
9c	Bessemer, 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Sn)
10d	Bessemer, 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, N)
22b	Bessemer, 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Sn)
15b	B. O. H., 0.1 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, As)
11d	B. O. H., 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, As)
12d	B. O. H., 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, As)
13c	B. O. H., 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, Al, Sn)
14c	B. O. H., 0.8 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Sn)
16c	B. O. H., 1.0 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
19c	A. O. H., 0.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
20c	A. O. H., 0.4 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
21c	A. O. H., 0.6 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
34a	A. O. H., 0.8 C	C, Mn, P, S, Si, (Cu, Cr, Mo)
35a	A. O. H., 1.0 C	C, Mn, P, S, Si, (Cu, Cr, Al)
51a	Electric furnace, 1.2 C	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
65a	Acid electric	C, Mn, P, S, Si, (Cu, Ni, Cr, V, Sn)
100	Medium manganese	C, Mn, P, S, Si, (Cu, Ni, Cr, V)
105	High sulphur	C
30c	Chrome-vanadium	C, Mn, P, S, Si, Cr, V, (Cu, Ni)
32b	Chrome-nickel	C, Mn, P, S, Si, Cr, Ni, (Cu)
33b	Nickel	C, Mn, P, S, Si, Ni, (Cu, Cr, V)
50a	Chrome-tungsten-vanadium	C, Mn, P, S, Si, W, Cr, V, (Cu, Mo. Sn)
72a	Chrome-molybdenum	C, Mn, P, S, Si, Cr, Mo, (Cu, V)
73	Stainless	C, Mn, P, S, Si, Cr, (Cu, V, Mo)
101	18 Cr, 8 Ni	C, Mn, P, S, Si, Cr, Ni, (Cu, V, N, Mo)
106	Cr-Mo-Al (nitralloy "G")	C, Mn, P, S, Si, Cr, Mo, Al, (Cu, Ni, V, As, N)
111	Ni-Mo-Cr (SAE 4615)	C, Mn, P, S, Si, Cr, Ni, Mo, (Cu, V, As)

TABLE 115 — *Continued*

Irons

Sample Number	Name	Constituents Determined or Intended Use
4e	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, Sn, V)
5g	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V)
6d	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V, Sn)
7c	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V)
55a	Ingot iron	C, Mn, P, S, Si, Cu, (Ni, Cr, N, Al, Co, Sn)
74	Cast iron	C, Mn, P, S, Si, Ti, (Cu, Ni, Cr, V)
82	Nickel-chromium cast iron	C, Mn, P, S, Si, Cr, Ni, (Ti, Cu, V)
107	Nickel-molybdenum cast iron	C, Mn, P, S, Si, Ni, Mo, Cr, (V, Cu, Ti)
115	Nickel-chromium-copper cast iron	C, Mn, P, S, Si, Ni, Cr, Cu, (V, Mo)

Steel-making Alloys

57	Refined silicon	Complete analysis
58	Ferrosilicon (75% silicon)	" "
59	Ferrosilicon (50% silicon)	" "
61	Ferrovanadium (high carbon)	" "
64	Ferrochromium (high carbon)	" "
66	Spiegeleisen	" "
67	Manganese metal	" "
68	Ferromanganese	" "
75	Ferrotungsten	" "
90	Ferrophosphorus	Phosphorus
71	Calcium molybdate	Mo, Fe, Ti
116	Ferrotitanium (low carbon)	Ti, C, Si, Cr, V, Al
117	Ferrotitanium (high carbon)	Ti, C, Si, Cr, V, Al

Non-ferrous Alloys

86	Aluminum-base casting alloy	Complete analysis
53a	Bearing metal, lead base	" "
54a	Bearing metal, tin base	" "
63	Bearing metal, phosphor-bronze	" "
37b	Brass, sheet	" "
52	Bronze, cast	" "
62	Bronze, manganese	" "
94	Zinc-base, die-casting alloy	" "
95	Zinc-base, die-casting alloy	" "
96	Zinc-base, die-casting alloy	" "

TABLE 115 — *Continued*

Ores

Sample Number	Name	Constituents Determined or Intended Use
69	Bauxite	Complete analysis
26	Iron ore, crescent	Al_2O_3, CaO, MgO
29	Iron ore, magnetite	Complete analysis
28	Iron ore, norrie	Mn (low)
27b	Iron ore, sibley	SiO_2, P, Fe
25b	Manganese ore	Manganese, available oxygen
56a	Phosphate rock (Tennessee)	P_2O_5, Fe_2O_3, Al_2O_3, etc.
120	Phosphate Rock (Florida)	P_2O_5, Fe_2O_3, Al_2O_3, etc.
2a	Zinc ore	Zinc

Ceramic Materials

104	Burned magnesite	Complete analysis
76	Burned refractory (40% Al_2O_3),	" "
77	Burned refractory (60% Al_2O_3)	" "
78	Burned refractory (70% Al_2O_3)	" "
103	Chrome refractory	Cr_2O_3, SiO_2, Al_2O_3, FeO, CaO, MgO
97	Clay, flint	Complete analysis
98	Clay, plastic	" "
70	Feldspar, potash	" "
99	Feldspar, soda	" "
79	Fluorspar	" "
1a	Limestone, argillaceous	" "
88	Limestone, dolomitic	" "
92	Glass, low boron	B_2O_3
93	Glass, high boron	Complete analysis
89	Glass, lead-barium	" "
91	Glass, opal	" "
80	Glass, soda-lime	" "
81	Glass sand	Fe_2O_3, Al_2O_3, TiO_2, ZrO_2, CaO, MgO
102	Silica brick	Complete analysis
112	Silicon carbide	" "

Fineness Standards

46q	Cement (normal)	
47f	Cement (extra fine)	
114	Cement (turbidimetric standard)	

TABLE 115 — *Continued*

Melting-point Standards

Sample Number	Name	Constituents Determined or Intended Use
44c	Aluminum	660.2° C
45a	Copper	1083° C
49	Lead	327.3° C
42b	Tin	231.9° C
43b	Zinc	419.4° C

Thermoelectric Standards

Sample Number	Name	Constituents Determined or Intended Use
118	Alumel	emf vs. temperature
119	Chromel P	emf vs. temperature

Chemicals

Sample Number	Name	Constituents Determined or Intended Use
84	Acid potassium phthalate	Acidimetric value
39e	Benzoic acid	Acidimetric and calorimetric values
40c	Sodium oxalate	Oxidimetric value
83	Arsenic trioxide	Oxidimetric value
38b	Naphthalene	Calorimetric value
17	Sucrose (cane-sugar)	Calorimetric and saccharimetric values
41	Dextrose (glucose)	Reducing value

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